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RESEARCH ON METAL MATRIX COMPOSITES FOR NAVAL AIRCRAFT ENGINES.(U)

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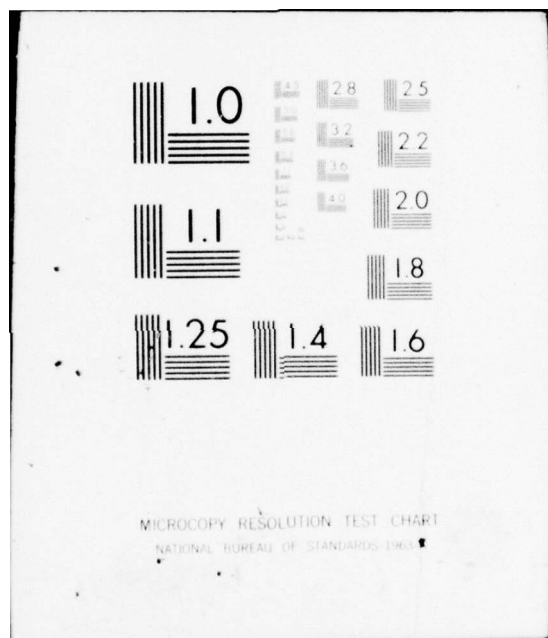
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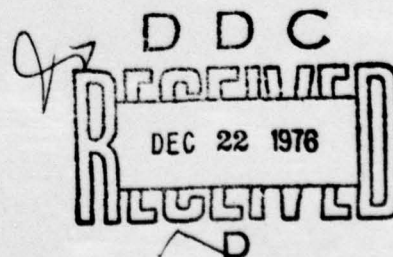
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A study of a Cr-25Cb-34Al (wt. %) directionally solidified alloy has verified the presence of a eutectic at the composition predicted by the computer model of Kaufman and Nesor. At a sufficiently high temperature gradient, it is possible to produce a fully aligned biphasic structure, having 50% volume fraction CbAl<sub>3</sub> fibers in a Cr-Cr<sub>2</sub>Al<sub>3</sub> matrix.

→ Preliminary weight gain oxidation tests at 2200°F, indicate the Cr-25Cb-34Al eutectic in the directionally solidified condition is superior in oxidation resistance to the carbide reinforced and ~~γ/γ'~~ directionally solidified eutectics currently being developed. However, the presence of a precipitated Cr<sub>2</sub>Al<sub>3</sub> phase in the Cr matrix appears to ~~make~~ this alloy too brittle to be structurally useful.

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## S U M M A R Y

## INTRODUCTION

Today one of the most promising approaches to increasing the strength of structural materials, particularly at elevated temperatures, is in composite strengthening wherein exceptionally high strength microdimensional materials of controlled orientation are incorporated in a suitable metal matrix. Unidirectional solidification of alloys of eutectic composition can produce "in-situ" composite materials having one or more high strength reinforcing phases in a metal matrix. These materials have the advantage of excellent thermal stability and the absence of fiber matrix interaction problems during fabrication. They are strong candidates for both the compressor stage (titanium base) and/or turbine stage blades and vanes of the jet engine. In the latter case directionally solidified eutectic alloys based on nickel and cobalt have already demonstrated a potential for increasing average metal operating temperature of 150°F to 200°F. These results have warranted leading aircraft engine firms to launch major research and development programs to develop these alloys as cost effective materials to improve engine performance. The alloys currently being developed, however, are limited by melting points below that of pure cobalt and nickel and by poor oxidation resistance.

This report covers the work over the four year period from November 1971 to November 1975 on Task WRO2204001 Research on Metal Matrix Composites for Naval Aircraft Engines. The purpose of this work unit is to identify, produce, and characterize new high melting point directionally solidified eutectic alloys which show promise for utilization in a 2100 - 2500°F engine environment. During the first year the emphasis was on titanium base eutectics for application at 1000°F in the compressor stage of the engine. The effort was shifted to the current objective when this area was seen to have a more significant pay-off.

## SUMMARY OF RESULTS

Eutectic binary alloys of titanium with iron, cobalt and nickel were directionally solidified on an electron beam zone melter. Metallographic examination revealed in the Ti-Fe system a matrix reinforced with 40 vol. % TiFe rods. The Ti-Co eutectic has a 48 vol. %  $\beta$  titanium dispersed phase in a FCC carbide type  $Ti_2Co$  matrix and the Ti-Ni eutectic structure consists of 30 vol. %  $\beta$  titanium fibers in a carbide type  $Ti_2Ni$  matrix. All the alloys were brittle when tested in tension. The Ti-Fe eutectic failed at 105,000 psi at 1000°F in a brittle manner due to the presence of a previously unobserved third phase.

Screening the microstructures of 22 different binary, ternary and quaternary columbium base systems has resulted in the identification of several eutectic systems whose morphology indicates possibilities as a structural material. These systems include Cb-Cr-Si, Cb-Cr-Ti, Cb-Si-Al, Cb-Si-Hf, Cb-Co-Ti, and Cb-Fe-Ti.



Cr-25Cb-34Al (wt. %) computer predicted eutectic alloy ingots have been directionally solidified at 0.25, 1, and 3 in/hr. Preliminary tests at 2200°F indicate that this alloy has an oxidation resistance superior to 75C,  $\gamma/\gamma'$ - $\delta$ , and COTAC 3, first generation directionally solidified eutectic alloys. Metallographic and spectrographic analysis of directionally solidified ingots of this alloy indicate that with a low temperature gradient at the solidifying interface (200°F/in) and a 1 in/hr. growth rate, there are large dendrites, misalignment of the fibers, changes in microstructure over the length of the ingot, and a decrease in chromium content from the first portion of the ingot to freeze to the final part. Apparently, the Cr-25Cb-34Al eutectic composition is located on a monovariant eutectic trough sloping downward in temperature toward a quasi-binary  $\text{Cr}_2\text{Al}_3$ - $\text{CbAl}_3$  eutectic at the aluminum rich end of the system.

At a higher gradient (500°F/in) and the same growth rate (1 in/hr.), the structure stabilizes producing well aligned  $\text{CbAl}_3$  fibers (50 v/o) in a Cr- $\text{Cr}_2\text{Al}_3$  matrix. The larger  $\text{CbAl}_3$  fibers in the center of finer  $\text{CbAl}_3$  fiber colonies initiate brittle cracks which propagate easily through the surrounding fibers and Cr- $\text{Cr}_2\text{Al}_3$  matrix. Changes in growth rate and composition did not suppress this brittle behavior.

#### CONCLUSIONS

1. Of the three different titanium base binary eutectic alloys studied the Ti-TiFe eutectic offers the best potential as a structural material for applications up to 1000°F. More research is needed, however, to identify and eliminate the cause of brittleness in the titanium matrix.
2. A technique has been developed for screening many multicomponent alloys for potentially useful directionally solidified eutectic alloys.
3. The computer analysis used to identify the Cr-25Cb-34Al eutectic alloy appears to be successful as far as yielding a prediction of eutectic composition. Although the oxidation resistance of this alloy looks promising, its strength appears unsuitable for structural applications.

#### RECOMMENDATIONS

The Davison and Rice model has demonstrated its usefulness in predicting the monovariant eutectic trough in the Cb-Cr-Si system and can be easily utilized with a programmable calculator. However, the more highly sophisticated Kaufman and Nesor model has been demonstrated on the Cr-Cb-Al eutectic as being fairly accurate in its prediction in this system and since it is now available on a time-sharing basis at a relatively low cost, it should be used to assist in identifying other potential ternary eutectic systems. This model would be particularly valuable if expanded to quaternary systems.

The screening techniques developed in this program should be continued and applied to other potential high temperature eutectic systems.

#### FUTURE PLANS

More study will be made of the columbium base eutectic systems identified as having possibly useful microstructures. Studies of columbium ternary and quaternary systems having boron and carbon additions will also be made. Other refractory metal base systems will be screened in a manner similar to the columbium base alloys. Nickel, cobalt and iron base eutectics having a composition based on the results of a Battelle study sponsored by NAVAIR will be melted in buttons and made into ingots to be used for directional solidification.



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## B A C K G R O U N D

In recent years, there has been considerable interest in the development of composite materials for aircraft structural application. Graphite/epoxy and metal matrix composites are well developed and have been applied to a variety of aircraft structures. High strength filaments embedded in the matrix give these materials high modulus and/or strength to weight ratios in the direction of the reinforcement. Metal matrix composites offer possible advantages over the organic matrix composites because of their potential for increased ductility and higher temperature capability. Considerable effort has gone into the development of aluminum and titanium matrix composites. The titanium matrix offers the potential of higher strength, modulus and temperature capability than the aluminum. The metal matrix composites have been much more difficult to fabricate than those with an organic matrix.

Unidirectional eutectic solidification offers several advantages as a method of preparing titanium matrix composites. Since the reinforcement is grown with the matrix there are no lay-up problems or fiber matrix interactions. Also, because the interface between the reinforcing phase and the matrix phase is usually formed at close to equilibrium conditions, it is very stable and microstructures have been produced that do not change at temperatures close to their melting point, reference (a). Eutectics have been grown with ductile metal matrices and reinforcing whiskers having strengths in excess of one million psi, reference (b).

Although limited to the eutectic systems that nature provides, it is still possible to vary the volume percent, size, and even morphology of the reinforcing phase by control of solidification parameters, purity and alloy content. Conventional heat-treating techniques and mechanical working, references (a), (b), (c), (d), and (e), are also available to enhance the properties of the matrix and the reinforcing phase.

Only a limited amount of work has been reported on titanium matrix eutectics. The systems studied have included Ti-TiB, Ti-Ti<sub>5</sub>Ge<sub>3</sub> and Ti-Ti<sub>5</sub>Si<sub>3</sub> all reported by Crossman and Yue, references (f) and (g). They reported that the TiB formed as a mixture of whiskers and blades in an  $\alpha$  titanium matrix. Due to the low volume percent of this phase there was no significant reinforcement. On the other hand, they found that the Ti<sub>5</sub>Si<sub>3</sub> and Ti<sub>5</sub>Ge<sub>3</sub> formed a eutectic having 31 and 34 volume percent, respectively, reinforcing fibrous phase in an  $\alpha$  titanium matrix. They concluded that the eutectic with the Ti<sub>5</sub>Si<sub>3</sub> fibers showed a considerable improvement over existing commercial alloys in Young's modulus, compressive yield strength, and creep strength.

Based on a survey of published phase diagrams, references (h), (i), and (j), it was decided that binary eutectics of titanium with iron, cobalt and nickel would be directionally solidified, morphology and composition of phases identified, and their strength characteristics determined. Calculations indicated that the volume fraction of the intermetallic phase could vary from 40% for Ti-Fe to 75% for Ti-Ni with Ti-Co intermediate at 50%. There is also a possibility of alloying between the iron, cobalt and nickel to vary morphology



and volume fraction of the intermetallic in the titanium matrix since TiFe, TiCo and TiNi have the same crystal structure and TiFe<sub>2</sub>, TiCo<sub>2</sub> and TiNi<sub>2</sub> also have the same structure.

The titanium base eutectics were seen to have a possibility for application as structural members in aircraft or as the compressor blades in the jet engine. However, work at United Technologies and General Electric in the United States and O.N.E.R.A. in France has indicated the potential of directionally solidified eutectics for use as turbine blades in the hot stage of the jet engine. These "in-situ" composites have already demonstrated a capability for increasing metal temperatures by 150 to 200°F in comparison with the best commercially available alloys today, reference (k). The payoff has been seen to be sufficient to warrant major development efforts by both United Technologies and General Electric. The alloys currently being developed, however, have poor oxidation resistance and melting points below that of pure nickel and cobalt. Therefore, there is a need for new eutectic systems which will overcome these limitations.

Accordingly, the effort in this program was shifted from exploring titanium base eutectics to one involving screening and evaluation of high temperature multicomponent eutectic systems having higher melting points and/or superior oxidation resistance. The screening program has focused initially on columbium base ternary and quaternary alloys systems but other refractory metal base systems will be studied. It is recognized that a coating system would probably be required for refractory metals, but that suitable alloying may slow down oxidation of the base metal if there should be a coating failure. In addition to screening of the refractory metal base eutectic systems, other high temperature eutectic compositions are being evaluated for morphology, oxidation resistance, and mechanical properties. Specifically, a Cr-25Cb-34Al (wt. %) eutectic, predicted with computer analysis by Kaufman and H. Nesor, reference (l), has been directionally solidified and evaluated. They predicted this alloy having a melting point of 2400°F, would be a good "in-situ" composite since a hard CbAl<sub>3</sub> phase would reinforce a Cr-10Cb-25Al (wt. %) matrix.

The work on the titanium alloys was reported at the Conference on In-Situ Composites held in Lakeville, Connecticut in September, 1972 and published in a National Materials Advisory Board Publication on the conference, reference (m), and is incorporated in this report. Subsequent work on these alloys was reported in a Work Unit Quarterly Status Report, April, 1973, reference (n) and the First and Second Quarterly Progress Reports for FY-74, references (o) and (p). The screening of the columbium base eutectics has been reported in the Work Unit Quarterly Status Report, the Quarterly Progress Reports for FY-74, and Quarterly Progress Reports for FY-75, references (n), (o), (p), (q), (r), (s), (t), and (u). This report summarizes this work as well. The above mentioned quarterly progress reports, starting with the second one also describes the work on the Cr-25Cb-34Al alloy and is incorporated in this report. A memorandum from April 1973 also describes work on this alloy, reference (v). Most of the study of the Cr-25Cb-34Al eutectic is summarized in a paper presented at the Conference on In-Situ Composites - II and is included in this report, reference (w).

## EXPERIMENTAL PROCEDURE

## MATERIALS

All the materials were in the form of solid chunks, flakes, shot, wire or rod. Table I is a list of the elements used in this study and their suppliers.

## EQUIPMENT

Several different furnaces were utilized during the course of this study. A Burrell High Temperature Electric Furnace (maximum temperature 2650°F), with a horizontal alumina tube and silicon carbide resistance elements, was operated with a continuous flow of argon for the initial melting of the titanium base eutectic rods for directional solidification. The initial alloying of the titanium buttons and slow cooling of some of the columbium alloy buttons was in a platinum wound resistance element, vertical tube furnace. It is fully described in references (x) and (y). The argon atmosphere was introduced through a water cooled, gas tight cap at the top which had a small (1/4 inch diameter) glass port for observation of the melt. The melt itself was contained in a 3/4 inch diameter alumina crucible which rested on an alumina thermocouple protection tube. This tube extended through the open bottom of the furnace and was clamped to a Syntron vibrator, the vibrations of which helped to stir the melt.

After the initial titanium studies all of the melting and some of the slow cooling studies were done in a "System VII" General Purpose Metallurgical Vacuum Facility, produced by Vacuum Industries, Inc. In this equipment, power is applied to the melt through a non-consumable electrode in a positive pressure argon atmosphere. Buttons were melted in a water cooled hearth having circular depressions 1/2 inch diameter by 1/4 inch deep. Rods were prepared by melting buttons in another water cooled hearth having a trough 3/8 inch wide by 4 inches long. Slow cooling experiments are done in this facility by removing the electrode assembly and water cooled hearth and replacing them with graphite resistance elements which can provide temperatures up to 4000°F. A mechanical pump, oil diffusion pump vacuum pumping systems has maintained pressures of 1 to  $5 \times 10^{-5}$  torr when melting alloys at temperatures of 3400°F. Temperatures are controlled and monitored with two W/5 Re - W/26 Re thermocouples sheathed in beryllia, tubes.

Directional solidification was accomplished in an electron beam zone melting unit and a resistance furnace directional solidification unit. All of the titanium alloys and some of the Cr-Cb-Al alloy rods were directionally solidified on the electron beam unit as described in reference (m). A vacuum of  $2 \times 10^{-7}$  to  $2 \times 10^{-6}$  torr was maintained for the titanium alloys using an ion pumping system.

The original directional solidification unit has been described in reference (z) and was first used for the directional solidification of aluminum base eutectics. After several modifications the furnace is now a Model PCA-10, molybdenum wound, resistance furnace manufactured by IMANCO, and capable of temperatures up to 3200°F. The booster coil described in reference (z) which helped to control and maintain a steeper temperature gradient was replaced with a molybdenum wound element for directional solidification of the higher gradient, Cr-Cb-Al eutectic alloys described in this report. Also, a nickel pedestal was

added to the drive system to provide a steeper more constant temperature gradient as compared to the previous system, where the crucible was pulled by a wire into the chill zone. A recent calibration run indicated that the temperature gradient was increasing as the ingot entered the chill zone.

#### ALLOY SELECTION

The compositions for the binary titanium and columbium base eutectic alloys were selected on the basis of published phase diagrams, references (h), (i), (j), and (ab). In cases where the buttons did not show a complete eutectic structure, additional alloys of varying compositions were melted and their microstructures examined to pinpoint the exact eutectic composition. The elements to be added to the columbium base ternary and quaternary eutectic alloys include; Fe, Co, B and C (form eutectics with Cb), Cr and Si (form eutectics with Cb and may improve oxidation resistance) and Al, Ti, Hf and Ni (may improve oxidation resistance and/or improve morphology of eutectic phase. The initial compositions in a system have been selected on the basis of intuitive projections from the component binary systems. Also used was a relatively simple computer technique developed by Davison and Rice, reference (aa), which they have shown to produce data in good agreement with experimental results in the Al-Cu-Mg system. This model has been programmed for the Wang calculator. The composition of the Cr-Cb-Al eutectic being studied as part of this program was selected on the basis of a more sophisticated computer analysis done by Kaufman and Nesor, reference (l).

#### ALLOYING

The ingredients for the alloys were weighed to an accuracy of 0.001 grams resulting in an accuracy of at least 0.01% depending on the total weight of the melt. Alloy buttons for the initial titanium base eutectic study were melted in the platinum wound resistance furnace, previously described in this report, under an argon atmosphere. During this initial study, ingots for directional solidification of Ti-(Fe, Ni and Co) alloys were melted in the silicon carbide resistance furnace as described in reference (m). All the melts of the titanium alloys in both the platinum resistance furnace and the silicon carbide furnace were contained in alumina crucibles at temperatures of 2200 to 2600°F at least 900°F below the melting points of the constituent elements. This is probably why there was no significant crucible reactions even though conventional titanium alloys are highly reactive with all the conventional refractories, reference (ac).

It was necessary to maintain good physical contact with the alloying ingredients since the contact points between the titanium and the iron, cobalt or nickel were where the eutectic melting reaction would originate. In order to minimize crucible reactions the alloys were kept in the molten state for times ranging from 10 to 20 minutes.

Initially titanium rods (1/8 inch diameter by 4 inches long) for directional solidification were alloyed in aluminum oxide boats under an argon atmosphere. The charge consisted of 1/8 inch diameter titanium rods with a strip or strips of iron, cobalt, or nickel distributed along the length of the rods so that the ratio of alloying elements was roughly constant. This was done to maintain a uniform composition the length of the ingot. There appeared to be very little



interaction between the melt and crucible as evidenced by the relative ease with which the rod was separated from the boat and the only slightly grayish appearance of the aluminum oxide that had been in contact with the molten metal. In addition, there was no metallographic evidence of contamination from the crucible. Oxide caused by exposure of the solidified ingot to the atmosphere, while being removed from the furnace, and possible surface contamination from the boat was removed by grinding with a rubber wheel.

The arc melting facility was used for the melting of all subsequent titanium base eutectics, the columbium screening program alloys and the Cr-Cb-Al eutectic alloys. Special techniques were developed for alloying high melting (columbium) constituents with low melting ones such as aluminum without excessive loss of low melting constituent.

Once alloyed on the first melt, the buttons were turned over and remelted at least four times to ensure complete homogeneity. If the buttons were to be used for metallographic studies, on the last melt, the power to the arc was gradually cut back so as to reduce the cooling rate and prepare a coarser microstructure. Rods were turned over and remelted at least two times in the arc furnace, and provided the charge for the electron beam zone melter or the directional solidification unit.

#### SLOW COOLING STUDIES

A procedure was developed for slow cooling previously arc melted buttons of promising eutectic alloys to form coarser microstructures and determine melting points. The coarser microstructure was useful in identifying the morphology of the phases in the eutectic. The melting point determinations aided in evaluating the potential usefulness of the alloy as a high temperature material and were used in the calibration of the directional solidification unit. Initially samples were slow cooled in the platinum resistance furnace, but after acquisition of the graphite resistance heating elements, the buttons were cooled in the General Purpose Metallurgical Vacuum Facility which is capable of higher temperatures. Melting point calibrations were done by heating pure metals having known melting points and observing at what apparent temperature liquid first appeared. Copper, silicon, and nickel served as standards in the platinum resistance furnace and copper, nickel, iron, titanium and zirconium were melted as standards in the graphite resistance furnace. The melting points were measured at a heating rate of 3 - 5°F/min. Cooling rates of 3°F/min. were utilized to prepare the coarse microstructure. This procedure made it possible to maintain very good control of the heating and cooling rates.

#### DIRECTIONAL SOLIDIFICATION

An electron beam zone melting unit was used to directionally solidify all of the titanium base eutectic rods. The floating zone technique insured no problem with crucible contamination and the high vacuum provided a very pure if not purifying environment. The stainless steel chamber of the system was pumped with a 1200 l/s ion pump and roughed down with liquid nitrogen sorption pumps,

thus providing a clean vacuum, free from contamination caused by back streaming oil vapors. The vacuum during melting ranged from  $2 \times 10^{-7}$  to  $2 \times 10^{-6}$  torr. A beam voltage from 1.2 to 1.8 KV and a beam current from 23 to 50 ma, depending on the alloy of the rod and the vacuum in the chamber, was necessary to create a stable molten zone. Initially, passes were made from the bottom to the top of the rod at a speed of 1 in./hr. for the first half of the traverse and 15 in./hr. for the remainder of the distance. To maintain the liquid zone at the highest speed it was necessary to increase the beam voltage by approximately 0.3 KV. In the subsequent phase of the titanium study arc melted rods of the Ti-32Fe eutectic were given two passes at 1 in./hr. in the electron beam zone melter. As described in reference (r), three rods of the computer predicted, Cr-25Cb-34Al eutectic alloy were directionally solidified on the electron beam zone melter at 1 in./hr. and 3 in./hr. Argon was bled into the chamber lowering the normally high vacuum from  $10^{-7}$  torr to  $10^{-4}$  torr to minimize volatilization of Al from the molten zone.

Cr-25Cb-34Al rods were prepared in the directional solidification unit as described in reference (s). Arc melted rods of the correct composition were melted in an alumina crucible under an argon atmosphere. Growth rates of 0.25, 1, and 3 in./hr. were used to produce rods 3/8 in. in diameter and up to 4-1/4 inches long. Superheats from 100 to 330°F were applied to the melt resulting in a maximum temperature of 2900°F.

#### METALLOGRAPHY

All directionally solidified rods were etched, given a macroscopic examination and photographed for future reference. This was done so that correlations could be made with microstructure and gross inhomogeneities such as growth fluctuations, undissolved ingredients and changes in macrostructure. Sections were cut from these rods in the longitudinal and transverse directions, and also from buttons, tensile specimens and oxidation specimens. They were prepared for microscopic examination by conventional metallographic techniques. The titanium base alloys were etched by immersion in a solution of 10% HF, 5% HNO<sub>3</sub> and 85% water. All the other eutectics were etched in the same manner in a 10% HF, 40% HNO<sub>3</sub> 50% water solution. The titanium etchant was such that the titanium rich phase was attacked in preference to the intermetallic constituents. The  $\alpha$  phase of titanium was differentiated from the  $\beta$  phase by its birefringence under polarized light, reference (ad). Quite often, columbium base eutectics would have some undissolved columbium in them making it possible to differentiate the columbium rich phases from the intermetallic phases by their appearance under the microscope. Phase volume fraction was determined by applying a point count method to photomicrographs of transverse sections of directionally solidified samples.

Some of the metallographic samples were also examined with the electron microprobe analyzer. The titanium base eutectics were scanned for titanium, iron, cobalt, and nickel; and the Cr-25Cb-34Al alloy was scanned for chromium, columbium and aluminum. Both fixed beam-specimen translation, resulting in a trace of elemental intensity versus distance, and fixed time counting (scalar), where the counts relative to elemental intensity were recorded at a fixed position on the surface. Where possible, specimens were examined which had



regions of undissolved titanium and columbium and gradually increasing concentrations of the other element or elements. These titanium rich or columbium rich regions served as internal standards for purposes of concentration comparison.

The other halves of the broken tensile specimens not used for metallographic studies were mounted and examined in a 30KV Scanning Electron Microscope. The resulting fractographs were evaluated on the basis of evidence of ductility or brittleness and other topographical features. Also, a Scanning Electron Microscope - Energy Dispersive X-ray Analysis (SEM - EDAX) was made of the phases present in one of the Cr-25Cb-34Al (wt. %) eutectic alloy ingots directionally solidified at 1 in./hr. in a gradient of 200°F/in. This same rod was analyzed by emission spectrography at 1 in. intervals along its length.

#### OXIDATION TESTING

Samples of the Cr-25Cb-34Al eutectic alloy were given an isothermal weight gain oxidation test at 2200°F for periods of 5 hours and 60 hours. Flat pieces (approximately 1/2 in. x 1/4 in. x .05 in.) were cut from the arc melted rods and directionally solidified on the electron beam zone melter. Samples were taken from both the zone melted portion and the un-melted portion of the rod for purposes of comparison. Pieces of Hastelloy X, which is noted for its good oxidation resistance, were also included in the test to provide baseline data. The surfaces of all the samples were polished on 600 grit emery paper, cleaned in acetone, weighed and placed in previously dried alumina crucibles and tested as described in reference (ae). During the 50 hour test, an overnight power failure resulted in a temperature drop-off to 1450°F before it was discovered the next morning and brought back up to temperature. To compensate for this perturbation the test was extended to the next day resulting in a total exposure to 2200°F of 60 hours along with the 8-1/2 hour period of cool down to 1450°F and a 2-1/2 hour time to return to 2200°F. After exposure, all the samples were again weighed in their crucibles and transverse sections were cut from them for metallographic examination.

#### MECHANICAL TESTING

After directional solidification, the rods were etched to determine any macrofeatures such as evidence of directional reinforcement and to aid in selecting the sections for mechanical testing. Reduced sections, 1/8 in. in diameter by 3/4 in. long were ground in the slowly solidified and the quickly solidified portions of the rods directionally solidified during the first phase of the titanium base eutectic study as reported in reference (m).

Because of their brittle nature, the rods were held gently against a rubber base grinding wheel and slowly turned to reduce their gage sections. After grinding, the portions of the rod containing the reduced section were cut apart and pulled in tension in an Instron testing machine. Self-aligning, split collet grips supported the shoulders of the specimens for testing. The specimens were pulled at a crosshead speed of .01 in./min. and the load recorded as a function of time with a strip chart recorder. Tensile specimens were ground in the shop from the Ti-32Fe eutectic rods solidified during the second

phase of the titanium study and tested as described above but at 1000°F in air. Due to their extreme brittleness only a few of the Cr-25Cb-34Al eutectic samples were successfully ground for tensile testing and these samples broke on setting up in the testing machine.

## R E S U L T S

Ti-Ti<sub>2</sub>Co EUTECTIC

In the first phase of the titanium program it had appeared that when 28 wt. % of cobalt was added to titanium to form a eutectic as indicated in published phase diagrams, reference (h) and (i), very little if any eutectic could be detected in the microstructure. After examining a series of buttons it seemed that the eutectic composition was somewhere between 32 and 33 wt. % cobalt. These buttons had been melted in the platinum resistance furnace. A series of buttons were melted in the arc furnace and metallographic examination of these indicated the eutectic was less than 31 wt. %. Figure 1 shows photomicrographs of sections from a portion of a 33.5 wt. % cobalt rod grown at the slow speed (1 in./hr.) in the electron beam zone melter.

There were dendrites in this rod and sections were selected that were most free of dendrites to try to produce the structures most characteristic of the eutectic, not perturbed by dendrites. The transverse section, Figure 1(a), shows a mixed structure of rods and lamellae. The lamellae appear to curve around the rods in some places and appear in straight parallel arrays in other areas. This seems to be a transition between a lamellar and a rod like morphology. The average diameter of the rods and thickness of the lamellae is 2 microns and there appears to be ~48 volume % of this phase. Microprobe analysis, consideration of the phase diagram and etching behavior indicates that the dark dispersed phase is  $\beta$  Ti and the white matrix phase is Ti<sub>2</sub>Co. The longitudinal section of this portion as shown in Figure 1(b), indicates some directionality in this structure.

A transverse section as shown in Figure 2(a) at the higher growth speed (15 in./hr.) shows basically the same type of structure, but the particles are finer, on the order of 0.5 micron. Figure 2(b), a longitudinal section through a portion of another Ti-Ti<sub>2</sub>Co rod grown at 15 in./hr., has regions where the eutectic forms a complex lamellar structure similar to that seen in Al-Si and Al-Ge directionally solidified eutectics, references (z), (af), (ag), and (ah). Samples from the Ti-Ti<sub>2</sub>Co rods broke in a brittle manner at stresses from 10,000 to 20,000 psi.

Ti-Ti<sub>2</sub>Ni EUTECTIC

As in the case of the Ti-Ti<sub>2</sub>Co eutectic, when an ingot of Ti-Ni was alloyed with 28.5 wt. % Ni as indicated in published phase diagrams, references (h) and (i), only a little eutectic could be found in the microstructure. Also, as with the Ti-Ti<sub>2</sub>Co eutectic, a series of buttons were melted at various compositions. As a result of this initial phase of the titanium study, the eutectic composition was reported in reference (m) as between 33 and 35 wt. % nickel. After this report as with the Ti-Ti<sub>2</sub>Co alloys, a series of buttons were melted in the arc furnace and metallographic examination of sections from these buttons indicated the eutectic was between 29 and 30 wt. % nickel. There were many highly dendritic areas so sections for metallographic analysis were selected as free from dendrites as possible to try to avoid perturbation from the dendrites.



Both Figures 3(a) and 3(b) are photomicrographs of sections from the portion of the Ti-Ti<sub>2</sub>Ni rod zone melted at 1 in./hr. Although Figure 3(a) is a longitudinal section, it does have a portion which appears to be transverse to the growth direction of the rods and is characteristic of rods seen in transverse section. The average diameter of the rods is 2 microns and they are 30 vol. % of the alloy. Their fibrous nature is quite apparent in Figure 3(b). The intersecting white spines of the matrix are similar to the Ti-Ti<sub>2</sub>Co eutectic grown at fast speeds as shown in Figure 2(b). In this case, however, there is no evidence of platelets or a lamellar structure. Similar to Ti-Ti<sub>2</sub>Co, the dark phase appears to be  $\beta$  titanium in a matrix of Ti<sub>2</sub>Ni. This conclusion is based on microprobe analysis, the phase diagram, and etching behavior. The  $\beta$  titanium itself appears to be a two or three phase structure. Examination under polarized light reveals small grains, barely resolved at 1200X, having the birefringence characteristic of  $\alpha$  titanium, reference (ad). A portion of a Ti-Ti<sub>2</sub>Ni eutectic rod which had been heated above the eutectoid temperature and rapidly cooled did not have this characteristic indicating that the  $\alpha$  had transformed back to  $\beta$  and the cooling was fast enough to prevent  $\alpha$  titanium from reforming. There also appears to be some dark spots in the  $\beta$  titanium which may be Ti<sub>2</sub>Ni precipitate.

Figure 4 is a section from a portion of the Ti-Ti<sub>2</sub>Ni eutectic rod solidified at 15 in./hr. The magnification here is twice that of the other photographs (1200X) so it represents rods having a very small diameter probably less than .5 microns. In this photograph the tendency to form platelets is quite apparent, also, other areas of the specimen showed the rods forming regular patterns as in Figure 3.

Samples from these Ti-Ti<sub>2</sub>Ni rods also failed in a brittle manner at stresses between 10,000 and 20,000 psi.

#### Ti-TiFe EUTECTIC

Examination of the microstructure of the Ti-Fe eutectic revealed a few small dendrites but a predominately eutectic structure at a composition of 32 wt. % Fe as indicated in published phase diagrams, reference (j). Rods grown at 1 in./hr. had some relatively large eutectic grains. The regular rod like nature of the discontinuous phase can be quite clearly seen in the transverse and longitudinal sections of the rod shown in Figure 5. Figure 5(c) is a photomicrograph of a transverse section at the intersection of three of these grains. The grain having the regular rods is the most characteristic and covered the largest region. The average diameter of these rods is 4 microns. A few grains had a more irregular rod structure or a rod and platelet structure as seen in the other two grains in Figure 5(c). The platelets appear to be thinner than the rods having a 2 micron thickness on the average. The transition between rods and platelets is quite apparent in this figure as rods appear to coalesce into platelets. Cline, et al, observed this type of structure in directionally solidified eutectics having molybdenum rods in a NiAl matrix and tungsten rods in a nickel matrix, reference (ai). They found that webs formed between faceted rods at branching faults giving rise to the platelets which is apparently the case here. Based on the conclusions from this work, the different orientation of the grain in Figure 5(c) caused the platelet structure to form.

Examination of the rods directionally solidified at 15 in./hr. reveals a colony type of structure as shown in Figure 6. This structure is much finer than that of the slowly solidified rods. The very fine fibers at the center of the colonies appear to have a diameter of 0.5 microns. Lamellae or platelets can be seen radiating outward from the center of the colonies. The colonies themselves appear to have a diameter of .05 mm. It has been well established that the higher growth rate will increase the tendency toward colony formation. Cline, et al, observed this type of structure in a NiAl-Cr 6.0 Mo eutectic and concluded that the faceted rod could not bend and grow normal to the solid-liquid interface, so it is forced to grow in platelets radiating out from the center with increasing thickness toward the edges of the cell, reference (ai).

A sample from a Ti-32Fe rod directionally solidified at 1 in./hr., tested in tension at room temperature failed at 45,000 psi with a brittle fracture. A photomicrograph, Figure 7(a), of a metallographic section perpendicular to the fracture surface shows the brittle nature of both the matrix and the fiber. This was brought out more clearly in the scanning electron photomicrograph in Figure 7(b). The faceted nature of the fibers can also be seen quite clearly. A sample from a Ti-32Fe rod solidified at 15 in./hr. had a brittle failure at 90,000 psi when tested in tension at room temperature. The scanning electron photomicrograph of Figure 6(c) shows not only the colony structure of the higher growth rate but some possible ductility in the dimpling of the  $\beta$  titanium phase between the cleavage faceted TiFe radiating outward from the center of a eutectic colony.

Additional rods of Ti-32Fe were arc melted, instead of melting in the Burrel furnace and directionally solidified as before at 1 in./hr. As previously reported in reference (p), a specimen tested in air at 1000°F failed without ductility at 105,000 psi. Metallographic examination of these samples revealed that the premature brittle failure was caused by an unidentified third phase previously not observed in these alloys. Figures 7(c) and 7(d) are photomicrographs of a longitudinal section near the fracture surface of a sample broken at 1000°F showing the brittle nature of this phase and its role in initiating failure of the sample.

#### COLUMBIUM BASE EUTECTICS

An extensive number of binary, ternary and quaternary columbium base eutectic alloys were arc melted as 10 gram buttons and evaluated metallographically as previously reported in references (n), (o), (p), (q), (r), (s), (t), and (u). The amount of eutectic present in the microstructure, its morphology and based on morphology, its potential as a structural material was evaluated and is listed in Table II. A desirable morphology is considered to be either lamellar or the columbium metallic phase as the continuous phase. A more complex microstructure where there might be more than two phases present, was also considered worthy of future evaluation. Those alloys which had been slow cooled are also indicated in Table II. As a desirable morphology, the microstructure of the Cb-10Cr-5Si-35Ti (wt. %) alloy is a good example of a columbium matrix with an inter-metallic dispersed phase. Figure 8 is a photomicrograph of a section from an



arc melted button of this alloy. The undissolved columbium is seen blending into a columbium solid solution which surrounds the intermetallic discontinuous phase. The lamellar type of structure which should also be indicative of a promising structural material is exemplified by the Cb-35Fe-22Ti wt. % alloy shown in Figure 9. Slow cooling a button of this alloy resulted in a more complicated structure. The columbium appears as fibers in the center of the eutectic region but becomes lamellar adjacent to the columbium rich dendrite. More study is needed in this particular system.

Another alloy having this structure, the Cb-14Cr-57Hf (wt. %) did not seem as promising on slow cooling, because it then appeared as fibrous columbium in an intermetallic matrix and is shown in Figure 10. In a few alloys, there was an indication of a third phase or a more complex microstructure. Figure 11 is a photomicrograph of one of these alloys having a composition of Cb-38Cr-7Ti (wt. %).

The least promising alloys, most of which had an intermetallic continuous phase are also listed in Table II. The Cb-22Fe-4Al (wt. %) alloy has this type of structure and is shown in Figure 12. The brittle nature of the matrix phase is indicated by the cracks which stop at the metallic phase and then continue on the other side.

There were problems in melting the Cb-Cr-Ti alloy in the platinum furnace. The Cb-Cr-Ti-Al alloy was successfully melted but only the intermetallic phase could be resolved in the microstructure.

Compositions of ternary and quaternary columbium base eutectic alloys for arc melted buttons were selected on the basis of inferred projections of monovariant eutectic troughs from the component binary systems. The Davison and Rice model for predicting monovariant eutectic troughs in ternary systems was applied to the Cb-Cr-Si system, reference (s). Monovariant eutectic lines were projected from the columbium rich end of the Cb-Si and Cb-Cr binary systems. The ternary interaction parameters were initially assumed to be "0" but at the intersection of the two projected monovariant eutectics, there was a discrepancy of almost 200°F in temperature. By an iterative technique the interaction parameters of both the Cb-Si and Cb-Cr based monovariant eutectics were varied until an interaction parameter was found that resulted in an intersection of both temperature and composition.

#### Cr-25Cb-34Al ALLOY

Progress on the Cr-25Cb-34Al alloy has been reported in references (p), (q), (r), (s), (t), (u), (v), and (w), and is summarized here. To arc melt buttons of these alloys, it was found necessary to first alloy the columbium and chromium before adding the aluminum. Otherwise, not all the columbium entered into solution. Upon examination of the arc melted buttons, the composition appeared to be 100% eutectic as predicted (reference (1)), and to have a lamellar morphology as shown in Figure 13(a). Halves of the buttons were remelted in both the platinum resistance furnace and graphite furnace and slow cooled at 3°F per minute to develop a coarser microstructure.

Examination of the platinum resistance melted, slow cooled sample revealed a mixture of  $\text{CbAl}_3$  lamellae and fibers with large block like  $\text{CbAl}_3$  crystals in the centers of some of the grains, Figure 13(b). A needle-like precipitate, Figure 13(c), can be seen in the chromium rich matrix. The melting point of this alloy was observed to be between 2444 and 2490°F, as compared to the melting point minimum of 2400°F, predicted by Kaufman and Nesor, reference (1).

Nine buttons at various compositions around the predicted eutectic point were arc melted and examined under the microscope. This was done to define more accurately the phases present in the microstructure, the range of compositions resulting in a eutectic structure, variations in microstructure caused by changes in composition, and as a basis for identifying shifts in composition due to directional solidification of the rods. The location of these alloys on the ternary phase diagram and the computer predicted monovariant eutectic troughs and minimum melting point are shown in Figure 14. The identification of the alloys is listed in Table III along with the characteristic microstructure. Figures showing representative photomicrographs are also listed in Table III. The partial binary Cr-Al phase diagram with the computer predicted phase boundaries, reference (1), and those reported in the literature, reference (ab), is also depicted in this figure.

Examination of these buttons indicates a range of compositions from Cr-25Cb-34Al (wt. %) to Cr-48Cb-37Al (wt. %) where a lamellar eutectic structure may be retained without detrimental dendrite formation. The microstructures of the alloys richest in chromium, Samples #3 and #7, indicate that primary  $\alpha$  (Cr) solidified first then as solidification progressed the composition of the liquidus shifted toward the  $\alpha$ - $\tau$  ( $\text{CbAl}_3$ ) eutectic at a composition near Sample #1. This solidified with the eutectic structure similar to Sample #1. Due to the decreasing solubility of chromium for aluminum,  $\gamma$  ( $\text{Cr}_2\text{Al}_3$  having a  $\gamma$  brass crystal structure) precipitated out of solution. There is a strong similarity in the appearance of the precipitate in Samples #3 and #7 of this study and the precipitate identified as  $\gamma$  by Koster, et al, reference (aj), in their study. An occasional needle like lamellar phase also appears in the  $\alpha$  grains. Studies of the binary Cr-Al system indicate a solid state ordering reaction of  $\alpha$  transforming to a  $\beta$  body centered tetragonal  $\text{MoSi}_2$  type of structure at 1670°F, references (ai) and (ah). The needles seen in this study could be this  $\beta$  phase, because of similarity to the lamellar form shown by Koster, et al, reference (aj).

Examination of the microstructures of Samples #9 and #10 indicates that solidification could have occurred in a manner similar to Samples #3 and #7 but with the primary reaction being the peritectic between  $\alpha$  Cr and the melt to form  $\text{Cr}_2\text{Al}_3$ . A small amount of  $\text{CbAl}_3$  appears at the  $\text{Cr}_2\text{Al}_3$  grain boundaries, probably caused by the quasi-binary eutectic reaction between  $\text{Cr}_2\text{Al}_3$  and  $\text{CbAl}_3$ . This interpretation is supported by the observation of Bradley and Lu, reference (ak), and Koster, et al, reference (aj), who both indicated a peritectic reaction for the formation of  $\text{Cr}_2\text{Al}_3$  as opposed to the computer predicted eutectic reaction of Kaufman and Nesor, reference (1).

Samples #2 and #8 appear to show the formation of  $\text{Cr}_2\text{Al}_3$  and  $\text{CbAl}_3$  only, while Samples #4 and #5 have dendrites of  $\lambda$  which is reported by Hunt and Ramon, reference (a1), and also indicate through computer calculations of Kaufman and Nesor, reference (1), to be  $\text{Cb}(\text{CrAl})_2$  (hexagonal  $\text{MgZn}_2$ ) capable of dissolving up to 45 atomic percent aluminum. Sample #5 has a low concentration of  $\lambda$  dendrites but Sample #4 has significantly higher concentration of  $\lambda$ .

Two rods of the computer predicted, Cr-25Cb-34Al eutectic alloy were directionally solidified on the electron beam zone melter at 1 in./hr. and 3 in./hr. Argon was bled into the chamber lowering the normally high vacuum from  $10^{-7}$  torr to  $10^{-4}$  torr to minimize volatilization of aluminum from the molten zone. However, it was found impossible to maintain a liquid zone at a 1 in./hr. solidification rate due to excessive evaporation of the aluminum. Two rods of this alloy were grown successfully at 3 in./hr.

Metallographic examination of sections from these rods reveals that enough aluminum was lost to produce a predominately dendritic structure as seen in Figure 16(a). There is good alignment in the eutectic regions not disturbed by dendrites as shown in Figure 16(b). Cracking appears associated with the dendritic phase and fine cracks appear to propagate through the brittle phase in aligned eutectic regions but are interrupted by an apparently more ductile matrix phase as seen in Figure 16(b).

Six more ingots of Cr-25Cb-34Al were prepared with the directional solidification unit at a gradient of  $200^\circ\text{F}/\text{in.}$  Arc melted rods of the correct composition were melted in an alumina crucible under an argon atmosphere. No loss of aluminum occurred during melting as was the case with the previously directionally solidified rods processed in the vacuum of the electron beam zone melter. Growth rates of 1, and 3 in./hr. were used to produce rods 3/8 in. diameter and up to 4-1/4 in. long. Maximum temperatures (based on calibration runs) of the melt varied from  $2570^\circ\text{F}$  to  $2900^\circ\text{F}$  resulting in superheats from  $100^\circ\text{F}$  to  $330^\circ\text{F}$  above the melting point of the Cr-Cb-Al alloy. Even after exposure to melts at  $2900^\circ\text{F}$  at a growth rate of 1 in./hr., there was no significant crucible reaction. However, a melt temperature of  $2800^\circ\text{F}$  seemed optimal since lower temperatures resulted in more misalignment and higher temperatures than  $2800^\circ\text{F}$  did not improve the alignment.

The microstructures of sections from these ingots were interpreted with the assistance of published binary phase diagrams, the computer predicted ternary phase diagram, examination of previously melted buttons of known composition, and SEM-EDAX. The directionally solidified ingots appear to have several distinct regions each having its own characteristics. Figure 17 is a photomicrograph of an etched ingot showing these regions and photomicrographs of transverse sections characteristic of these regions. Figure 18 consists of photomicrographs and SEM's of sections from this ingot and table IV lists the SEM-EDAX data from these sections. Starting at the bottom of the ingot which solidified first, there is:

The Initial Region - Segregation of the highest melting constituents such as undissolved - Cb,  $\lambda\text{-Cb}(\text{CrAl})_2$  and  $\alpha\text{-Cr}$  creates dendritic structures which disrupt alignment of Cr-CbAl<sub>3</sub> inter-dendritic eutectic. As the melt progresses only  $\text{Cb}(\text{CrAl})_2$  dendrites and eutectic are observed. A photomicrograph



and SEM of this region can be seen in Figures 18(a) and 18(b). EDAX confirms the presence of  $\text{Cb}(\text{CrAl}_2)$  dendrites and a eutectic having  $\text{CbAl}_3$  fibers, blades, and lamellae in a chromium rich matrix. The analysis also indicates that the needle like phase may be  $\text{Cr}_2\text{Al}$ . Individual particles of  $\text{Cr}_2\text{Al}_3$  in the eutectic matrix and/or chromium dendrites could not be resolved. EDAX indicates the composition of the chromium rich dendrites present in the initial region to solidify as being at a location A in the Cr-Cb-Al ternary diagram, Figure 14, and the matrix of the eutectic, having a volume fraction of 80 percent  $\text{CbAl}_3$  blades and lamellae, as being close to this composition.

The Lamellar Region - The  $\text{Cb}(\text{CrAl}_2)$  dendrites diminish both in quantity and size. The eutectic appears as a mixture of  $\text{CbAl}_3$  lamellae, blades and fibers having a very high volume fraction in a Cr- $\text{Cr}_2\text{Al}_3$  matrix. There is good alignment within the eutectic phase.

The Complex Lamellar Region - No more  $\text{Cb}(\text{CrAl}_2)$  dendrites are present but the herringbone pattern of the  $\text{CbAl}_3$  phase does not result in good alignment, Figure 17.

The Fibrous Region - Large faceted  $\text{CbAl}_3$  crystals form and tend to be elongated in the growth direction but many form with their axis perpendicular to the growth direction. As can be seen in Figure 18, they seem to form from a coalescence of lamellar  $\text{CbAl}_3$ . Many smaller  $\text{CbAl}_3$  faceted fibers are seen around the large dendrites. As the end of the ingot is approached, these large dendrites seem to diminish and approach the size of the surrounding fibers. The  $\text{CbAl}_3$  fibers appear to occupy a smaller volume fraction of the matrix (50 percent) than the lamellar  $\text{CbAl}_3$ . SEM-EDAX places the composition of the Cr- $\text{Cr}_2\text{Al}_3$  matrix of the eutectic having a 50 percent volume fraction of  $\text{CbAl}_3$  fibers at location B, Figure 14, within 5 atomic percent of the composition of the predicted eutectic matrix. Analysis of the matrix of the last to solidify eutectic with a 16 percent volume fraction of  $\text{CbAl}_3$  fibers indicates its composition to be at position C in Figure 14, only a few atomic percent from the  $\text{Cr}_2\text{Al}_3$  composition.

At the end of the fibrous region, at the last portion to solidify, there is distinct transition from the eutectic having a volume fraction of 50 percent  $\text{CbAl}_3$  in a Cr- $\text{Cr}_2\text{Al}_3$  matrix to one having a volume fraction of 16 percent  $\text{CbAl}_3$  in a  $\text{Cr}_2\text{Al}_3$  matrix as shown in Figures 18(c) and 18(d). The photomicrograph, Figure 18(d), brings out clearly this transition. The SEM, Figure 18(e), shows the single phase nature of the matrix of the final portion to solidify and EDAX indicates that it is entirely  $\text{Cr}_2\text{Al}_3$  phase. The matrix of the high fraction  $\text{CbAl}_3$  eutectic adjacent to the last region to freeze, appears to be a Cr- $\text{Cr}_2\text{Al}_3$  mixture, but energy dispersive x-ray analysis could not determine if  $\text{Cr}_2\text{Al}$  was also present in the matrix. Extensive cracking in the completely  $\text{Cr}_2\text{Al}_3$  matrix eutectic but not present in the Cr- $\text{Cr}_2\text{Al}_3$  matrix eutectic, indicates that the Cr- $\text{Cr}_2\text{Al}_3$  is the more desirable structure.

A spectrographic analysis was also made of one of the ingots, the results of which are listed in Table V. Due to a lack of internal standards only a qualitative analysis could be made. These results indicate a decrease of chromium as the ingot solidified and either a constant Cb/Al ratio or a constant columbium or aluminum content the length of the ingot.

Additional ingots of the Cr-25Cb-34Al eutectic were prepared with the improved directional solidification unit having the higher 500°F/in. temperature gradient provided by the pedestal support for the crucible. These ingots had a uniform structure of well aligned CbAl<sub>3</sub> fiber in a Cr-Cr<sub>2</sub>Al<sub>3</sub> matrix their entire length, portions of which can be seen in Figure 19. The large CbAl<sub>3</sub> dendrites appear to align themselves in oriented arrays as can be seen in Figure 19(a). Within these arrays, the fine faceted fibers form a cellular structure with many of the colonies having a large faceted CbAl<sub>3</sub> dendrite in the center, surrounded by very fine CbAl<sub>3</sub> fibers having square or rectangular cross-sections. In Figure 19(b), the elongated eutectic grains can be seen in polarized light. It was also apparent from their birefringence in polarized light, that all the massive dendrites and fine fibers within one grain had the same crystallographic orientation. The CbAl<sub>3</sub> fibers occupy a volume fraction of 50 percent, as shown in Figure 19(e). A two phase matrix is also apparent, probably consisting of αCr with a Cr<sub>2</sub>Al<sub>3</sub> precipitate.

The temperature profile of the directional solidification unit was optimized by varying the power inputs to the main winding and booster coil resulting in a temperature gradient of 900°F/in. The growth rate for the computer predicted Cr-25Cb-34Al eutectic was reduced from 1.00 to .25 in./hr. resulting in a lamellar instead of fibrous microstructure, as can be seen in Figure 20. The composition of one ingot was shifted to Cr-30Cb-30Al to suppress Cr<sub>2</sub>Al<sub>3</sub> formation in the Cr matrix, but metallographic examination and microhardness measurements indicate that the matrix is still brittle.

#### Oxidation

For the oxidation studies, the results of the weight gain tests along with comparable data from other investigators for 73C, reference (am), COTAC 3, reference (an), γ'-δ, reference (an), and γ/γ'-δ, references (ae), (ao), and (an), in situ composites and Hastelloy X, reference (ae), as an oxidation resistant standard, are listed in Table VI.

The photomicrographs, Figure 21, of transverse sections taken from samples exposed for 5 hours at 2200°F show the difference in the oxidation mechanisms of the three samples. After exposure at 2200°F for 60 hours, the Hastelloy X appeared black and the inside of the crucible in which it rested was black also. The Cr-25Cb-34Al alloy was grayish white and the inside of the crucible was clean. The oxide appeared as fine powder from the Hastelloy X but as large flakes from the Cr-25Cb-34Al (as cast) and fewer finer flakes from the Cr-25Cb-34Al (directionally solidified at 3 in./hr.).

#### Mechanical Properties

Attempts were made to perform 2000°F tensile tests on samples of Cr-25Cb-34Al eutectic alloy ingots directionally solidified in a temperature gradient of 500°F/in. at a rate of 1 in./hr. No tensile data was obtained, however, due to failure of the samples during machining and handling or failure of the grips during testing. Metallographic examination of these samples revealed that cracking originated in the large CbAl<sub>3</sub> dendrites and then propagated through the rest of the material. This is indicated in the photomicrographs, Figure 22.

## DISCUSSION

## TITANIUM BASE EUTECTICS

Dependent on whether iron, cobalt or nickel is alloyed with titanium at its eutectic composition on the titanium rich side of the phase diagram, a range of structures is formed as a result of directional solidification. When iron is the alloying ingredient, titanium is the matrix phase with a 40 volume percent reinforcing intermetallic TiFe in rod or platelet form. At the other extreme is the Ti-Ni system having the intermetallic  $Ti_2Ni$  occupying 70 volume percent of the alloy becoming the matrix phase and the metallic titanium becoming the rod like dispersed phase. The Ti-Co eutectic represents a structure in between these two extremes, where at 52 volume percent, intermetallic  $Ti_2Co$  appears to be the matrix phase. However, the titanium discontinuous phase, although it is found as rods, also forms an interconnecting lamellar form almost becoming a continuous phase itself. This type of microstructure has been observed by others, reference (ap), and in work at NADC on other eutectic systems.

The intermetallic phase in the Ti-Fe system is the cubic TiFe which is homologueous with  $TiCo$  and  $TiNi$ , reference (aq). This means there is a potential for alloying cobalt and/or nickel with TiFe changing its properties including volume percent. The FCC  $Ti_2Fe$  did not form in the eutectics because at least 6 atomic percent oxygen is needed to stabilize this phase, reference (ar), and the high vacuum of the electron beam zone refiner prevented this from happening. On the other hand,  $Ti_2Co$  and  $Ti_2Ni$  did form in the eutectic with cobalt and nickel. This is true no doubt because these intermetallics do not need oxygen to stabilize them, reference (ar). Since  $Ti_2Fe$ , and  $Ti_2Co$  are isomorphous compounds, reference (ar), it may be possible to change the eutectic morphology by replacing some of the cobalt in  $Ti_2Co$  with iron.

The lack of ductility and low stresses for failure in the testing of the Ti- $Ti_2Co$  and Ti- $Ti_2Ni$  eutectics was caused by brittle failure in predominately intermetallic dendritic regions and is probably no indication of the strength of the eutectic. The Ti-TiFe eutectic also failed in a brittle manner and a crack near the fracture face can be seen in Figure 7(a). The manner in which the crack grows straight through the  $\beta$  titanium matrix as well as the TiFe fiber with only a slight deflection at the interface between the phases indicates a brittle matrix. The fractograph, Figure 6(c), of the fast grown Ti-TiFe indicates some ductility by the dimpling of the  $\beta$  titanium phase between the cleavage faceted TiFe radiating outward from the center of a eutectic colony. Tensile specimens more carefully machined would probably have better strength properties.

Of the three systems, the Ti-TiFe appears the most promising for strength properties because of a metallic matrix whose properties could possibly be improved by suitable heat treatment and/or alloying. The 40 volume percent TiFe rod like phase having a cubic crystal structure may make a good reinforcing phase. Other studies have shown that alloying of this phase with cobalt or nickel would tend to make it a more ductile intermetallic by increasing the electron to atom ratio and decreasing the directionality of its bonds making it more metallic, reference (ar). Therefore, there is a potential for strengthening this alloy.



The brittle failure of the Ti-32Fe samples tested at 1000°F raises more questions about the potential of this alloy. More research would be necessary to identify the cause of the embrittling third phase and also to improve the ductility of the  $\beta$  titanium matrix. However, coupling of results of current work on conventional  $\beta$  titanium alloys with more research on the Ti-TiFe eutectic of this work could well result in a structurally useful alloy up to 1000°F.

#### COLUMBIUM BASE EUTECTICS

During the course of this program, several methods have been developed for identifying promising eutectic alloys. Examination of arc melted buttons has been shown to be useful in determining whether a system contains a eutectic, giving a qualitative picture of how close the composition is to eutectic composition, and conveying some information about eutectic morphology. Slow cooling of buttons provides even more information in terms of melting point determination and better resolution of eutectic morphology. This appears to be a good backup technique for the study of more promising alloys selected from the arc melted buttons. Many columbium base eutectic systems have been rejected in this study and a few promising ones identified. The Cb-Cr-Si base alloy with the Ti and Fe as quaternary additions appear worthy of more study. Also, the Cb-Cr-Ti, Cb-Cr-Ti-Al, Cb-Si-Al, Cb-Si-Hf, Cb-Co-Ti and Cb-Ti-Fe systems should be investigated more. Columbium base systems having boron and carbon additions need to be screened. The Davison and Rice model for predicting monovariant eutectic troughs appears to have been successful in predicting the compositions of Cb-Cr-Si eutectics at the Cb corner of the ternary system.

#### Cr-25Cb-34Al EUTECTIC ALLOY

The results of the examination of the microstructure of the nine buttons at various compositions around the predicted eutectic point, coupled with the microscopic, SEM-EDAX, and spectrographic analysis of ingots directionally solidified at 200°F/in. has verified the presence of a eutectic at the composition predicted by the computer model of Kaufman and Nesor. Also, the composition of the matrix phase of this *in situ* composite was within 5 AT % of the predicted composition, position B in Figure 14. This alloy and a Hf-Cr-Ni eutectic investigated by Kim and Ashbrook, reference (as), are the first eutectics to be studied as a result of computer analysis and generally verify the predictions of Kaufman and Nesor, affirming their technique.

From observations made on these ingots, it appears that the solidification process for the Cr-25Cb-34Al eutectic alloy is not stable at a growth rate of 1 in./hr. and a low temperature gradient of 200°F/in. The alloy that first solidifies in the ingot is close to the composition of Sample #7 in Figure 14. As solidification progresses the composition of the remaining liquid moves through the eutectic composition near Sample #6 and the final portion to solidify is at a composition close to Sample #2, the quasi-binary eutectic between  $\text{Cr}_2\text{Al}_3$  and  $\text{CbAl}_3$ .

Evidently, there is a monovariant eutectic trough sloping downward from a composition in the region of Sample #1 toward the quasi-binary eutectic at Sample #2. Since it has been demonstrated that the steeper the slope of the

monovariant eutectic trough, the more difficult it is to maintain stable biphasic plain front growth, reference (at), and the predicted eutectic composition is not stable during solidification at low gradients, there must be no minimum in the monovariant eutectic trough at the postulated eutectic composition, reference (1).

Directional solidification at the highest temperature gradient has considerably improved the alignment of the fibers and has stabilized the microstructure so that it is uniform the length of the ingot. Other workers have shown, in both the 73C, (Co,Cr) - (C,Cr,Co)<sub>7</sub>C<sub>3</sub> system having a downward sloping monovariant eutectic trough, reference (au), and  $\gamma/\gamma'\delta$  which solidifies on a sloping bivariant eutectic surface, reference (av), that coupled biphasic growth over a range of compositions and temperatures, is possible.

The colony structure with the massive CbAl<sub>3</sub> dendrites similar to those observed in other systems such as the (Al,Cu) - Al<sub>3</sub>Ni eutectic, reference (aw), indicates that a higher temperature gradient and/or lower growth rate is needed to produce a fully composite structure. The high volume fraction of the CbAl<sub>3</sub> phase in the fibrous rather than lamellar form is caused by the decreasing solubility of chromium for both aluminum, reference (a), and columbium, reference (j). This type of behavior has been observed in other systems, references (m), (f), and (g), and is caused by diffusion of the excess constituents to the fiber during cooling. The high concentration of CbAl<sub>3</sub> fibers should help to increase the strength of this alloy and the decreasing solubility of  $\alpha$  Cr for both columbium and aluminum should suppress the formation of brittle Cr<sub>2</sub>Al<sub>3</sub> in favor of enlarging the diameter of the CbAl<sub>3</sub> fibers.

It is clear from the data that the oxidation resistance of the Cr-25Cb-34Al eutectic in the directionally solidified condition is superior to 73C,  $\gamma'\delta$ ,  $\gamma/\gamma'\delta$ , and COTAC-3, but not as good as Hastelloy X or sputter-coated 73C. It is interesting to note that, similar to a report of the results of oxidation studies on 73C, reference (am), the Cr-25Cb-34Al in the directionally solidified condition did not oxidize as much as in the arc melted condition. The preferential attack of the chromium matrix phase in the arc melted sample in contrast to the uniform rate of oxidation in the directionally solidified alloy as seen in Figure 21 may explain this difference in behavior. These tests are very limited but do indicate a potential for good oxidation resistance in this alloy.

A study of deformation mechanisms in massive CbAl<sub>3</sub> indicates that it is brittle at room temperature due to the fact that its only deformation mode is by the formation of twins which are very difficult to generate, reference (ax). The Cr-Cr<sub>2</sub>Al<sub>3</sub> matrix of the Cr-25Cb-34Al, although not as brittle as the all Cr<sub>2</sub>Al<sub>3</sub> matrix, still does not appear to have a good crack propagation resistance. Therefore, the elimination of the large CbAl<sub>3</sub> dendrites by higher temperature gradients or lower solidification rates may not result in an alloy with adequate ductility.

Large brittle dendrites of Al<sub>3</sub>Ni in a (Al,Cu) matrix of a monovariant directionally solidified eutectic, have also been observed to be responsible for premature brittle failure, reference (ax). There is some evidence of plastic shear deformation or twinning in the fine fibers (Figure 22). The Cr-Cr<sub>2</sub>Al<sub>3</sub> matrix of the Cr-25Cb-34Al does not appear to have good crack propagation

resistance. Therefore, the elimination of the large  $\text{CrAl}_3$  dendrites by higher temperature gradients or lower solidification rates may not result in an alloy with adequate ductility.

Variation in growth parameters and changes in composition based on the results of this study do not appear to eliminate the formation of brittle  $\text{Cr}_2\text{Al}_3$  in the chromium matrix of this in situ composite or improve its toughness. No additional study of this eutectic, therefore, appears warranted.



A C K N O W L E D G E M E N T S

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TABLE I  
PURITY OF STARTING ELEMENTS

<u>Material</u>	<u>Source</u>
99.95 % Al	Bram Metallurgical Chemical Co.
99.995 % Co	Bram Metallurgical Chemical Co.
99.999 % Cr	Bram Metallurgical Chemical Co.
99.5 % Hf	Bram Metallurgical Chemical Co.
99.999 % Si	Bram Metallurgical Chemical Co.
99.95 % Ti	Bram Metallurgical Chemical Co.
99.8 % Cb	Fansteel Metallurgical Corp.
99.90 % Fe	Plastic Metals Div. of Crane Corp.
99.9 % Ni	International Nickel Co.



TABLE II  
COLUMBIUM BASE EUTECTIC ALLOYS EXAMINED

<u>Alloy - Wt. %</u>	<u>Morphology</u>	<u>Potential</u>
Cb-30Cr 38Cr 38.5Cr 39.0 40Cr	Intermetallic Matrix	-
Cb-33Cr-9Si 21Cr-4Si 5Cr-10Si	Third Phase	+
Cb-10Cr-5Si-35Ti	Cb Matrix	+
Cb-20Cr-5Si-10Al 3Cr-5Si-2Al	Two Intermetallic Phases	-
Cb-3Cr-7Si-4Fe	Third Phase	+
Cb-20Cr-30Co	Intermetallic Matrix	-
Cb-20Cr-30Co-5Al	Intermetallic Matrix	-
Cb-50Cr-5Ti 38Cr-7Ti	Third Phase	+
Cb-45Cr-5Ti-10Al	Lamellar	+
Cb-30Cr-16Fe 21Cr-15Fe	Intermetallic Matrix	-
Cb-16Cr-54Hf 14Cr-57Hf 46Cr-38Hf	Lamellar Fibrous	+ -
Cb-2Si 4Si TSi 6Si 6.5Si 7Si 10Si 15Si	Intermetallic Matrix	-

TABLE II (cont'd)  
COLUMBIUM BASE EUTECTIC ALLOYS EXAMINED

<u>Alloy - Wt. %</u>	<u>Morphology</u>	<u>Potential</u>
Cb-18Si-18Fe 8Si-15Fe	Intermetallic Matrix	-
Cb-10Si-10Fe-30Ti 5Si-20Fe-10Ti 11Si-22Fe-33Ti	Intermetallic Matrix	-
Cb-8Si-15Fe-10Al 15Si-15Fe-10Al	Intermetallic Matrix	-
Cb-3Si-7Co	Intermetallic Matrix	-
Cb-5Si-10Ti 4Si-28Ti	Two Intermetallic Phases	-
Cb-8Si-8Al 4Si-5Al	Columbium Matrix	+
Cb-4Si-36Hf	Lamellar	+
Cb-24Co-13Ti	Complex	+
Cb-20Ti-15Fe 22Ti-35Fe 15Ti-43Fe	Lamellar Complex Fibrous	+
Cb-26Fe 27Fe 29Fe	Intermetallic Matrix	-
Cb-31Fe-4Al	Intermetallic Matrix	-

TABLE III  
Cr-Cb-Al ARC MELTED BUTTONS

<u>Sample No.</u>	<u>Composition (Wt. %)</u>	<u>Representative Photomicrograph</u>	<u>Phases Observed</u>
1 6	Cr-25Cb-34Al Cr-18Cb-37Al	Figure 13	Eutectic ( $\alpha, \beta, \gamma, \tau$ )
9 10	Cr-5Cb-40Al Cr-9Cb-42Al	Figure 15(a)	$\beta, \gamma$ + Eutectic ( $\gamma + \tau$ )
2 8	Cr-17Cb-43Al Cr-26Cb-37Al	Figure 15(b)	Primary $\gamma$ + Eutectic ( $\gamma + \tau$ )
3 7	Cr-12Cb-34Al Cr-25Cb-30Al	Figure 15(c)	Primary $\alpha(\beta, \gamma)$ + Eutectic ( $\alpha, \beta, \gamma + \tau$ )
4 5	Cr-39Cb-28Al Cr-32Cb-31Al	Figure 15(d)	Dendritic $\lambda$ + Eutectic ( $\alpha, \beta, \gamma + \tau$ )

Formulae Of Phases

$\alpha$  - Cr Solid Solution  
 $\beta$  -  $\text{Cr}_2\text{Al}$   
 $\gamma$  -  $\text{Cr}_2\text{Al}_3$   
 $\lambda$  -  $\text{Cb}(\text{Cr}, \text{Al})_2$   
 $\tau$  -  $\text{CbAl}_3$



TABLE IV

## SCANNING ELECTRON MICROSCOPE - ENERGY DISPERSIVE X-RAY ELEMENTAL ANALYSIS

<u>Sample Location</u>	<u>Phase</u>	<u>Element</u>	<u>Counts (300 Sec.)</u>	<u>Percent Of Total</u>	<u>Ratio</u>
Initial Region Longitudinal Section (Figure 18b)	Matrix Cr-Cr <sub>2</sub> Al <sub>3</sub>	Al	10,437	31.0	1
		Cb	1,346	4.0	-
		Cr	21,903	65.0	2
		Total	33,686		
	Needles Cr <sub>2</sub> Al	Al	11,158	34.3	1
		Cb	2,379	7.3	
		Cr	18,973	58.4	2
		Total	32,510		
	Fibers CbAl <sub>3</sub>	Al	31,203	64.1	2
		Cb	16,574	34.1	1
		Cr	881	1.8	
		Total	48,658		
	Dendrite Cb(CrAl) <sub>2</sub>	Al	13,924	32.3	5
		Cb	20,550	47.7	3
		Cr	8,560	19.9	2
		Total	43,034		
	Matrix Cr-Cr <sub>2</sub> Al <sub>3</sub>	Al	14,643	28.3	1
		Cb	1,536	3.0	
		Cr	35,466	68.7	2
		Total	51,645		
	Fiber CbAl <sub>3</sub>	Al	39,502	63.1	2
		Cb	22,247	35.5	1
		Cr	837	1.3	
		Total	62,586		
	Dendrite Cb(CrAl) <sub>2</sub>	Al	10,776	32.5	5
		Cb	15,758	47.6	3
		Cr	6,601	19.9	2
		Total	33,135		

TABLE IV (cont'd)  
SCANNING ELECTRON MICROSCOPE - ENERGY DISPERSIVE X-RAY ELEMENTAL ANALYSIS

Sample Location	Phase	Element	Counts (300 Sec.)	Percent Of Total	Ratio
Final Region Longitudinal Section (Figure 18e)	Matrix Cr-Cr <sub>2</sub> Al <sub>3</sub>	Al	9,242	36.5	1
		Cb	119	0.5	
		Cr	15,965	63.0	2
		Total	25,236		
	Matrix Cr <sub>2</sub> Al <sub>3</sub>	Al	18,224	55.6	3
		Cb	1,026	3.2	
		Cr	13,507	41.2	2
		Total	32,757		
	Dendritic Fiber CbAl <sub>3</sub>	Al	24,267	64.1	2
		Cb	12,823	33.8	1
		Cr	795	2.1	
		Total	37,885		
	Large Fiber CbAl <sub>3</sub>	Al	20,610	64.9	2
		Cb	10,781	34.0	1
		Cr	360	1.1	
		Total	31,751		

TABLE V

## QUALITATIVE EMISSION SPECTROGRAPHIC ANALYSIS OF Cr-25Cb-34Al INGOT

Location on Ingot (Distance From Bottom cm)	Ratio Transmittance	
	Al/ Cr	Cb/ Cr
Bottom	.51	.66
1	.42	.57
2	.40	.60
3	.38	.52
4	.36	.54
5	.38	.50
6	.33	.52
7 (Top)	.33	.49
Reverse Side Top	.32	.64
Button Top	.41	.57
Button Bottom	.50	.77

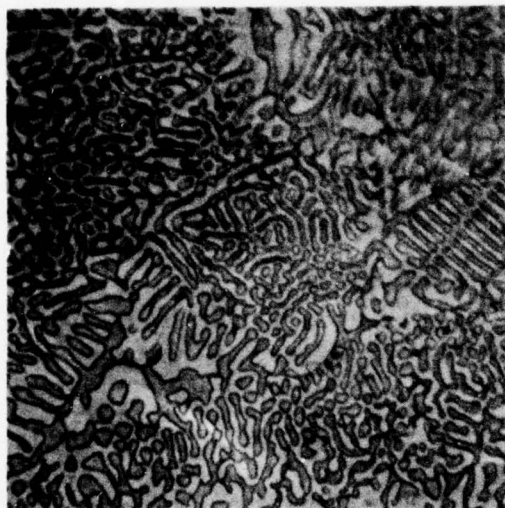
Lines Read Al 2575.10 A° 80 weight line  
 Cr 2381.48 A° 25 weight line  
 Cb 2376.40 A° 60 weight line



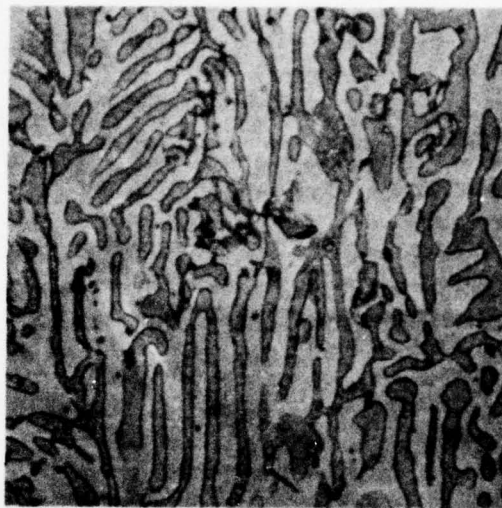
TABLE VI

SPECIFIC WEIGHT GAIN OF SEVERAL DIRECTIONALLY  
SOLIDIFIED EUTECTIC ALLOYS AND HASTELLOY X

<u>Alloy</u>	<u>Ref.</u>	<u>Temp-°F</u>	<u>Weight Gain - mg/cm<sup>2</sup></u>		
			<u>5 Hr.</u>	<u>50 Hr.</u>	<u>60 Hr.</u>
$\gamma'$ - $\delta$ (Ni-23.1Cb-4.4Al)	(an)	2012	3.0	20.0	22.0
COTAC-3 (Co-20Cr-10Ni-12.7Ta-0.75C)	(an)	2012	1.0	5.0	5.5
$\gamma/\gamma'$ - $\delta$ (Ni-19.7Cb-6 Cr-2.5Al)	(an)	2012	1.0	6.0	7.0
	(ae)	2192	3.5	7.0	7.5
73C (Co-41Cr-2.4C)					
Conventional Cast	(an)	2145	2.8	6.4	6.9
Directionally Solidified	(an)	2145	1.6	3.8	4.3
Sputtered Co, Al+Y	(an)	2050	0.6	1.7	1.8
Cr-25Cb-34Al					
As Cast	NADC	2200	0.8	-	5.9
Directionally Solidified	NADC	2200	0.3	-	3.1
Hastelloy X (Ni-22Cr-18.5Fe-Mo-1.5Co, 0.6 W-5Si-0.5Mn-0.1C)	(ae)	2192	-	1.5	1.6
	NADC	2200	0.5	-	2.1

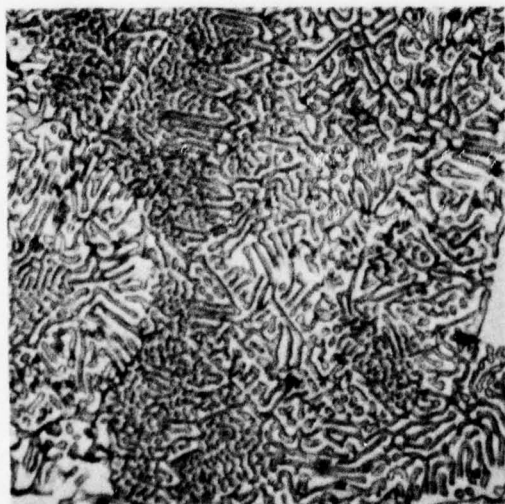


(a) Transverse Section

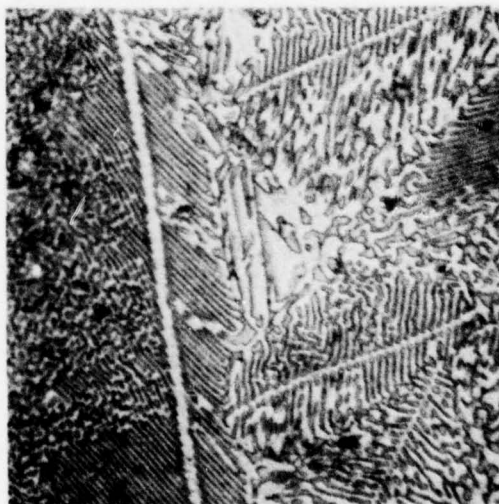


(b) Longitudinal Section

**Figure 1.** Ti-33.5 Co Rod Directionally Solidified at 1 in/hr.  
Magnification 640X

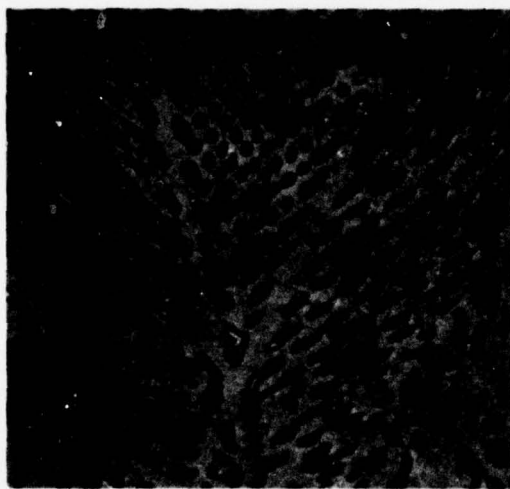


(a) Ti-33.5 Co Transverse Section

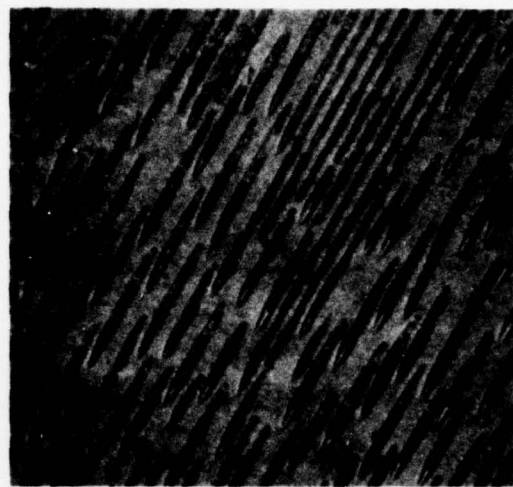


(b) Ti-34 Co Longitudinal Section

**Figure 2.** Ti-Co Rods Directionally Solidified at 15 in/hr.  
Magnification 640X



(a) Longitudinal Section



(b) Transverse Section

Figure 3. Ti-32Ni Rod Directionally Solidified at 1 in/hr.  
Magnification 640X

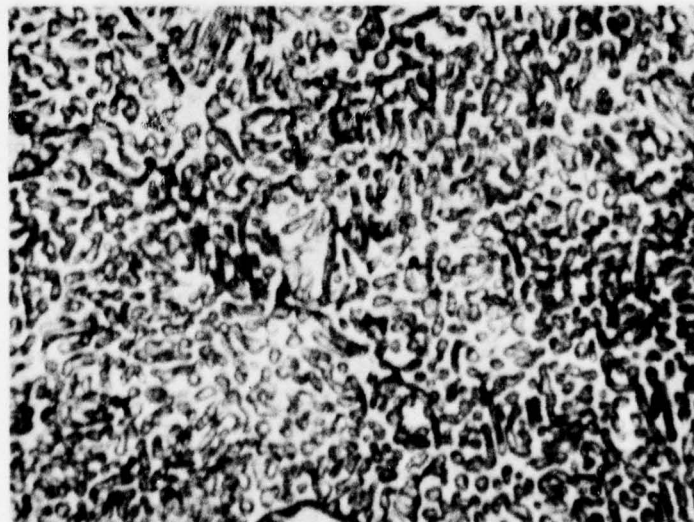
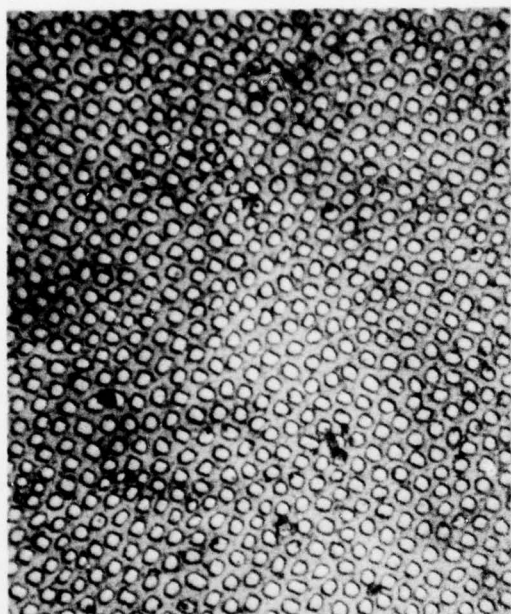
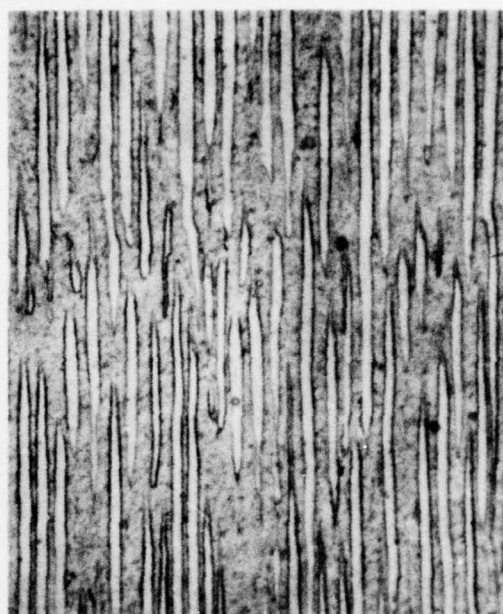


Figure 4. Ti-32Ni Rod Directionally Solidified at 15 in/hr.  
Magnification 1200X

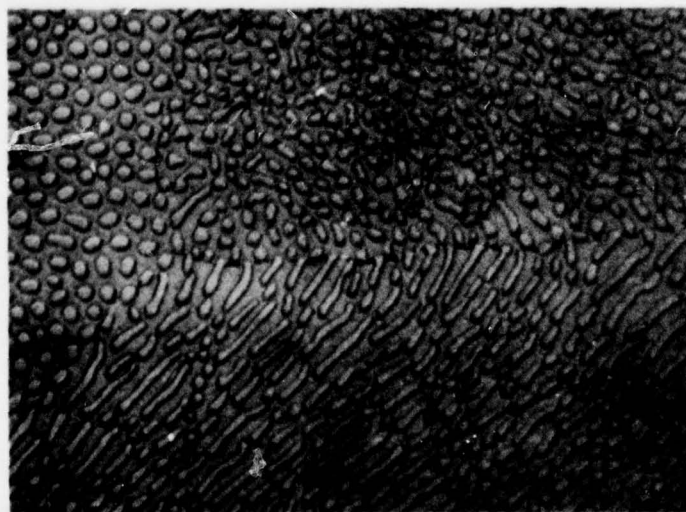




(a) Transverse Section



(b) Longitudinal Section

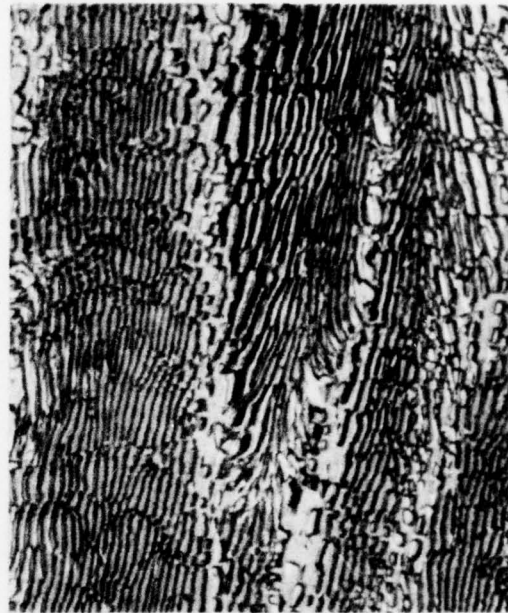


(c) Transverse Section of Three Eutectic Grains

Figure 5. Ti-32Fe Rod Directionally Solidified at 1 in/hr.  
Magnification 640X



(a) Transverse Section  
Magnification 640X

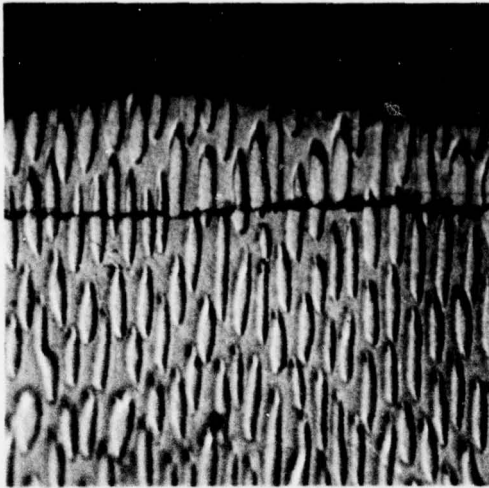


(b) Longitudinal Section  
Magnification 640X

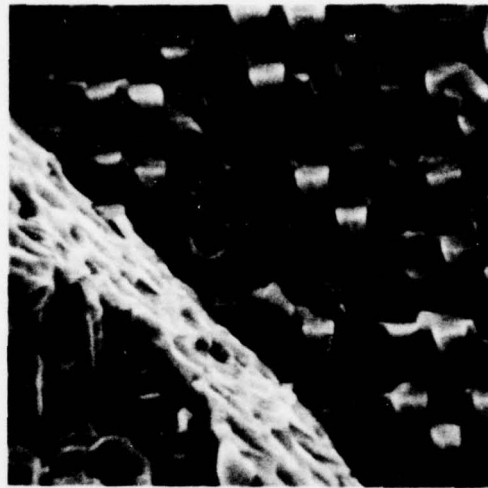


(c) Scanning Electron Micrograph of Fracture Surface  
Magnification 2000X

Figure 6. Ti-32Fe Rod Directionally Solidified at 15 in/hr.  
Eutectic Colony Microstructure

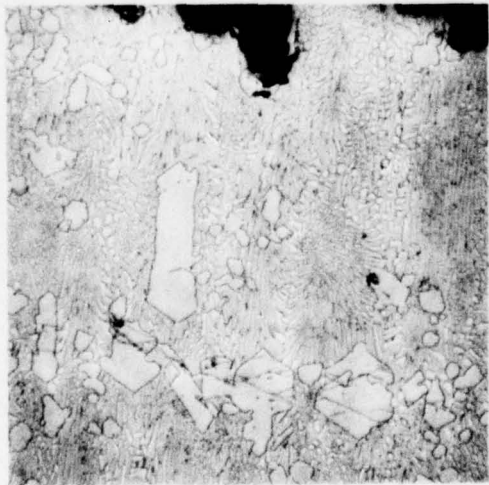


(a) Transverse Section  
Magnification 640X

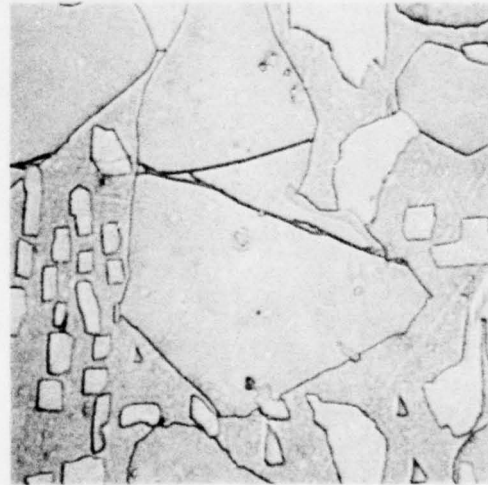


(b) Scanning Electron Micrograph  
of Fracture Surface  
Magnification 2000X

Rod Tested at Room Temperature



(c) Magnification 100X



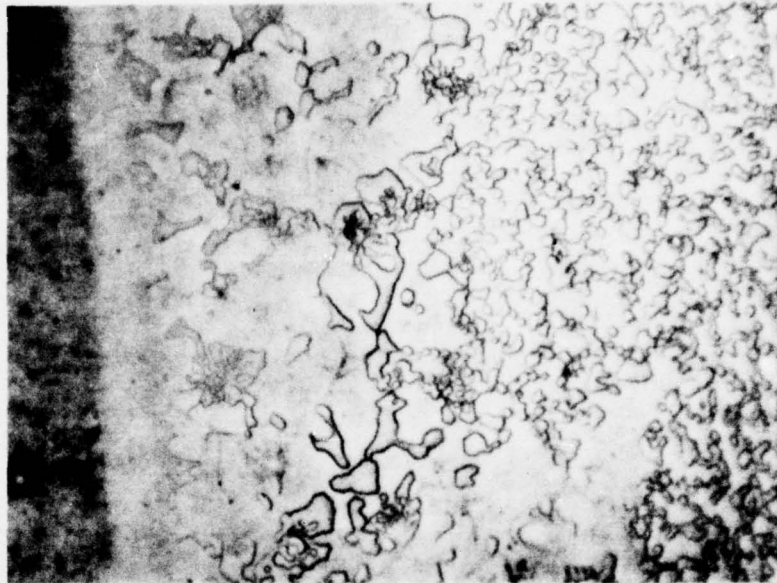
(d) Magnification 1000X

Rod Tested at 1000°F - Transverse Section

Figure 7. Ti-32Fe Rods Directionally Solidified at 1 in/hr.



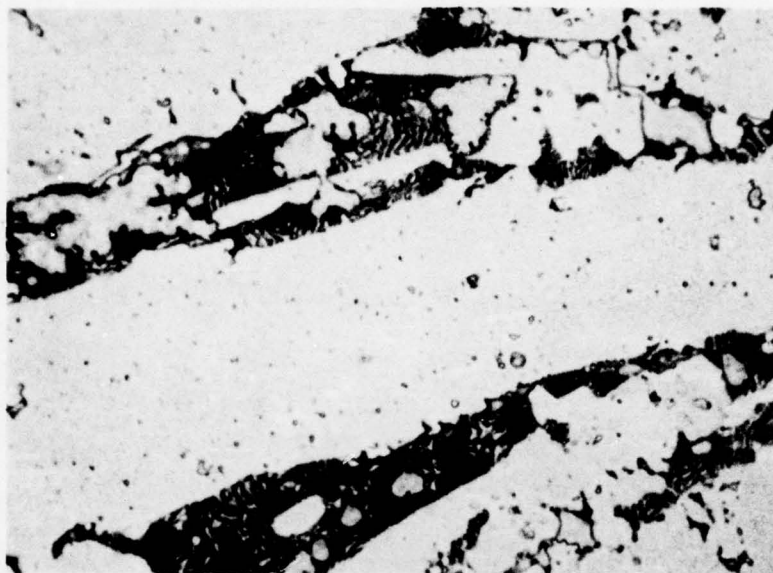
NADC-76217-30



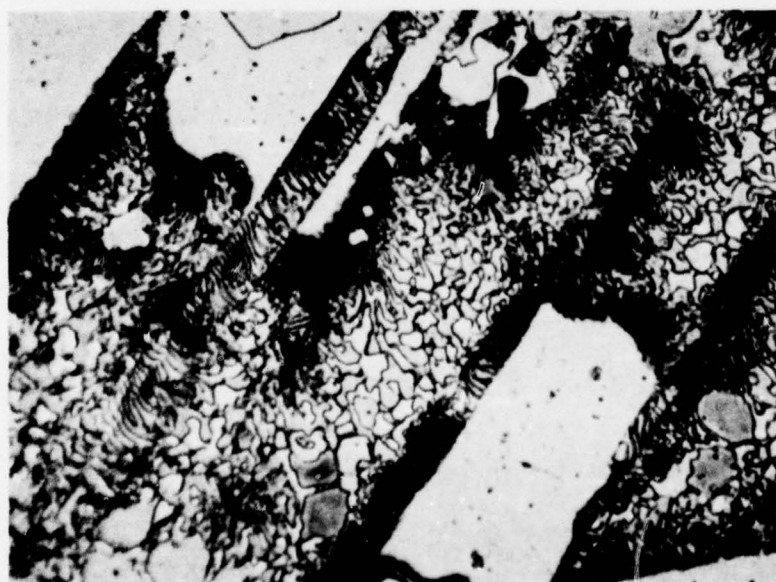
Pure  
Cb

Cb Matrix

Figure 8. Arc Melted Cb-10Cr-5Si-35Ti  
Magnification 1000X

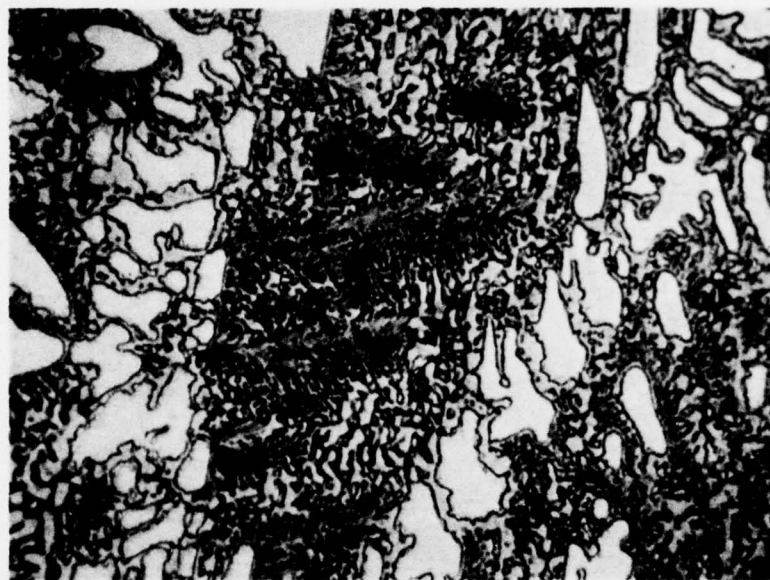


(a) Arc Melted

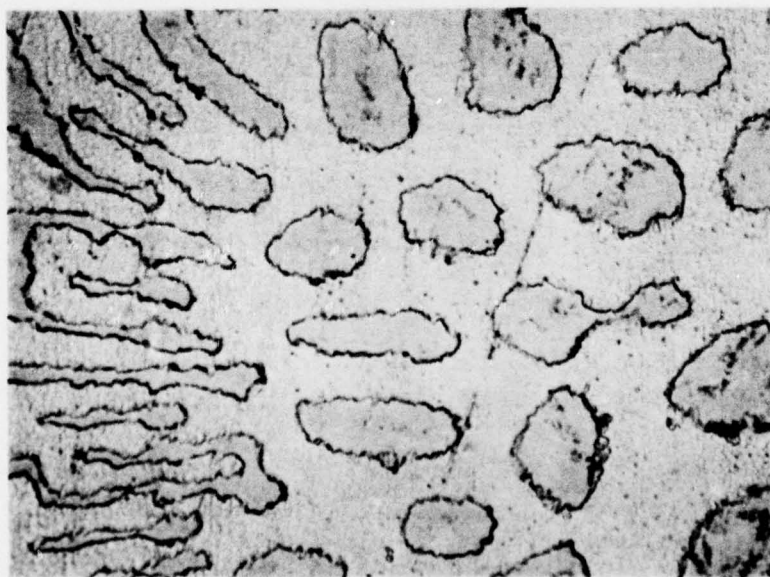


(b) Slow Cooled 30°F/min.

Figure 9. Arc Melted Cb-35Fe-22Ti  
Magnification 100CX



(a) Arc Melted



(b) Slow Cooled 3°F/min.

Figure 10. Arc Melted Cb-14Cr-57Hf  
Magnification 1000X



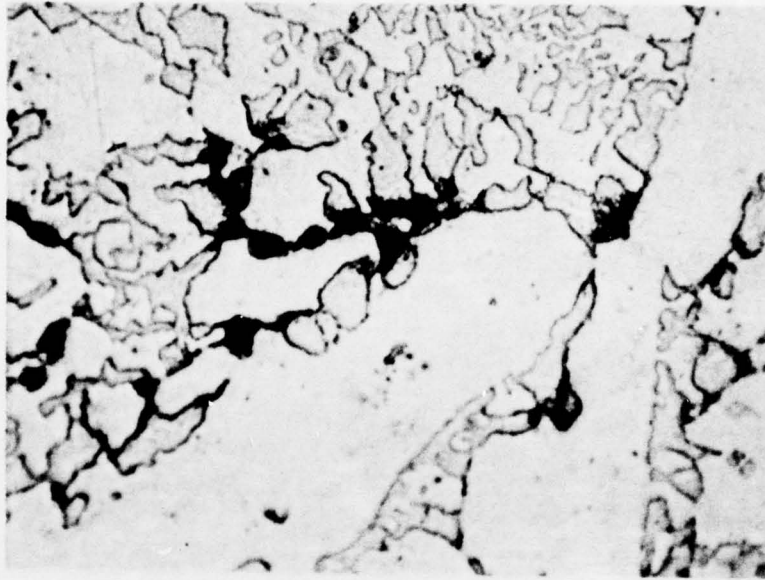
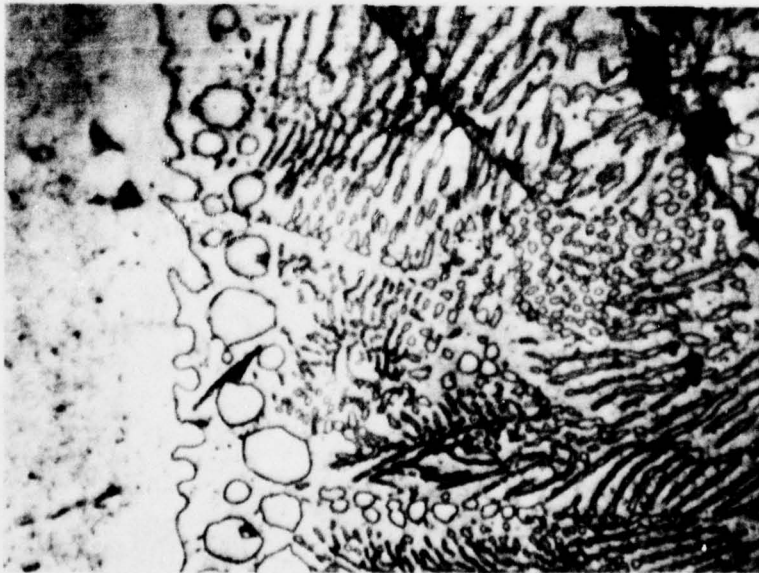
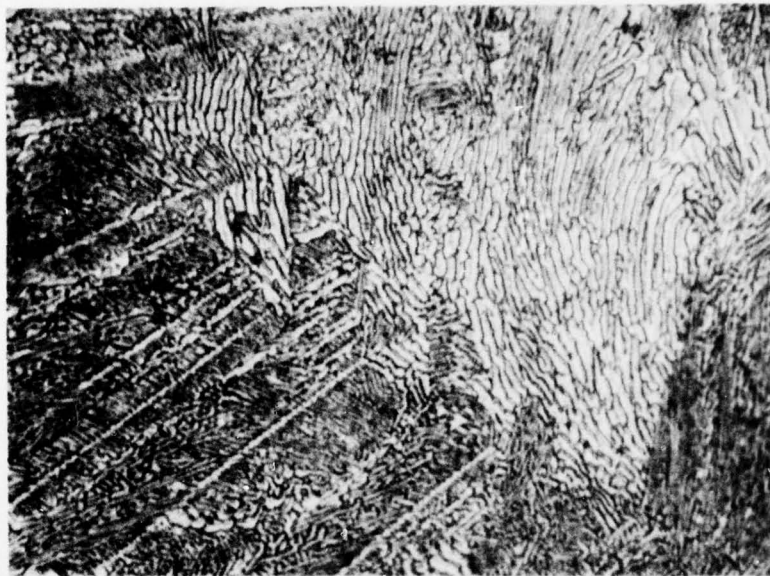


Figure 11. Arc Melted Cb-38Cr-7Ti  
Magnification 1000X

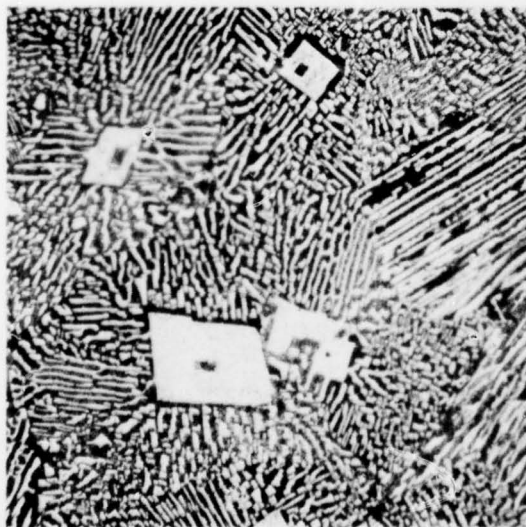


Cb Intermetallic Matrix

Figure 12. Arc Melted Cb-22Fe-4Al  
Magnification 1000X



(a) As Melted; Rapid Quench  
Magnification 1000X



(b) Slow Cool; 3°F/min  
Magnification 100X



(c) Slow Cool; 3°F/min.  
Magnification 1000X

Figure 13. Arc Melted Cr-25Cb-34Al

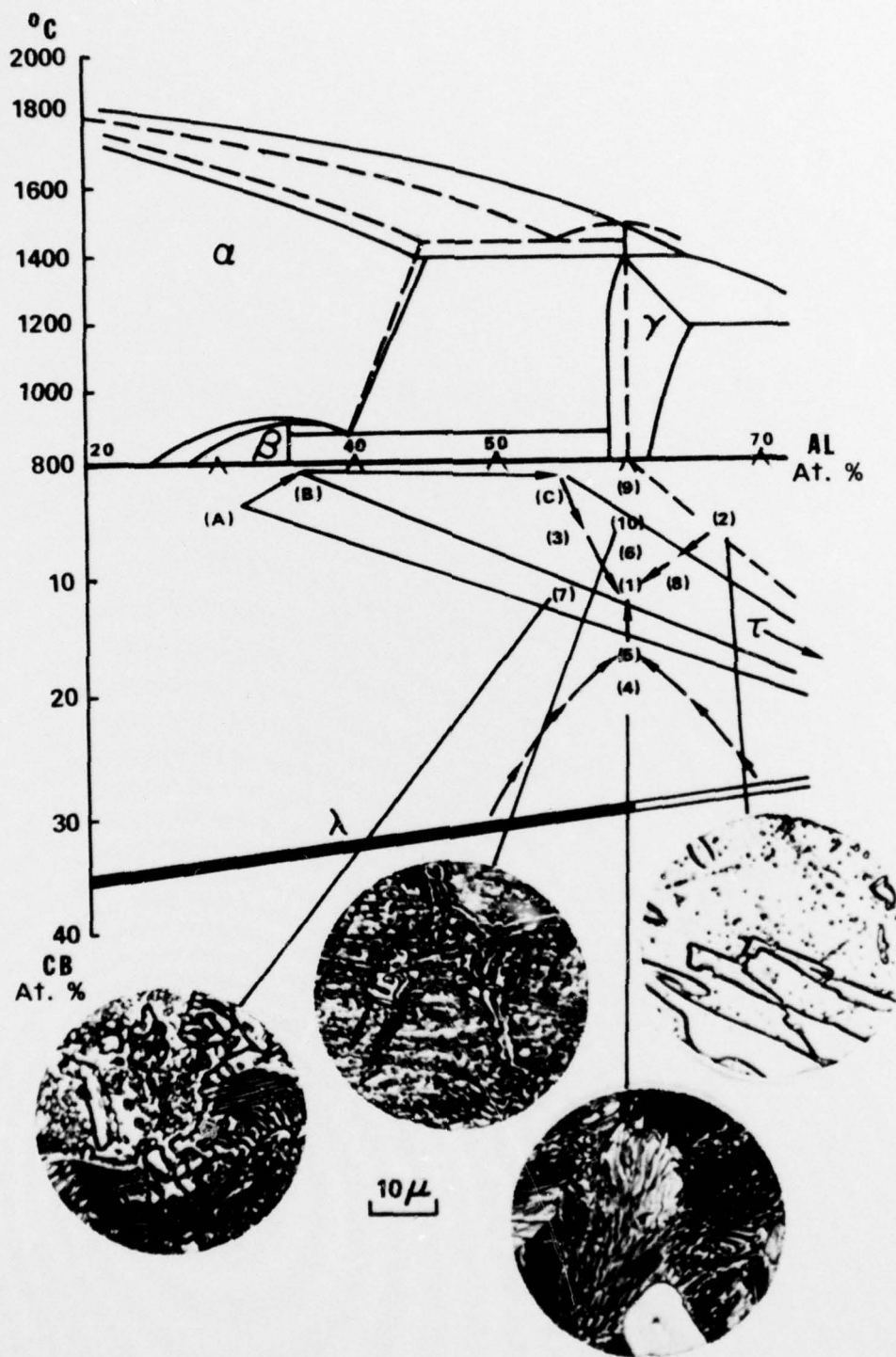


Figure 14. Partial Phase Diagrams of the Cr-Cb-Al System and Microstructures of Arc Melted Buttons





(a) Cr-9Cb-42Al  
(Sample No. 10)



(b) Cr-17Cb-34Al  
(Sample No. 2)

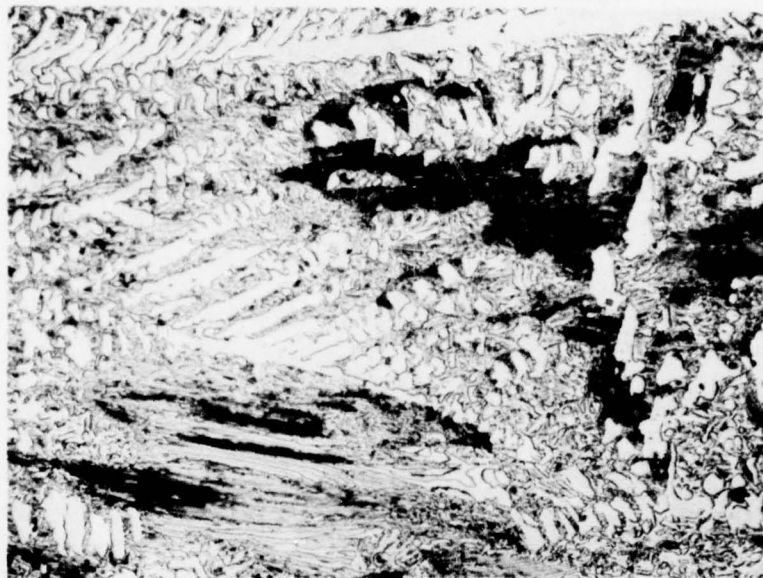


(c) Cr-12Cb-34Al  
(Sample No. 7)



(d) Cr-32Cb-31Al  
(Sample No. 4)

Figure 15. Arc Melted Cr-Cb-Al Alloys Magnification 1000X



(a) Magnification 100X



(b) Magnification 1000X

Figure 16. Longitudinal Section of Cr-25Cb-34Al  
Directionally Solidified at 3 in/hr.  
on the Electron Beam Zone Melter

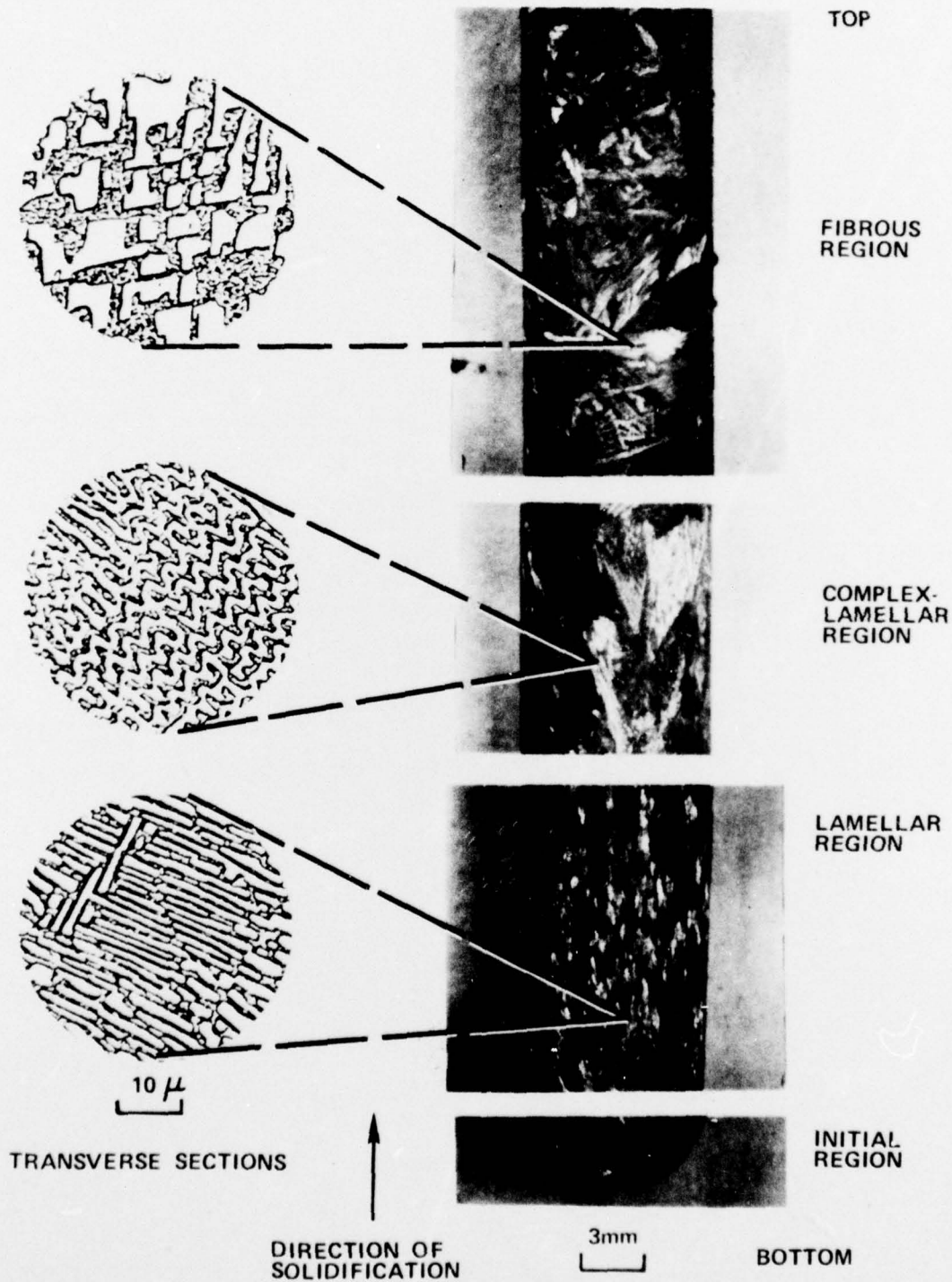
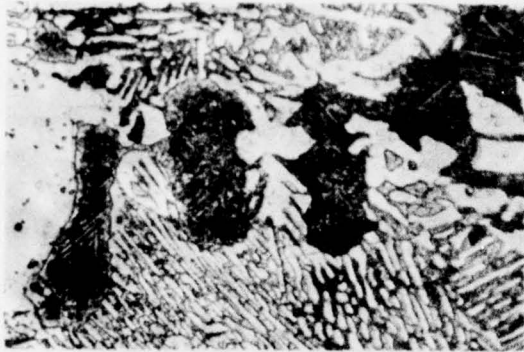
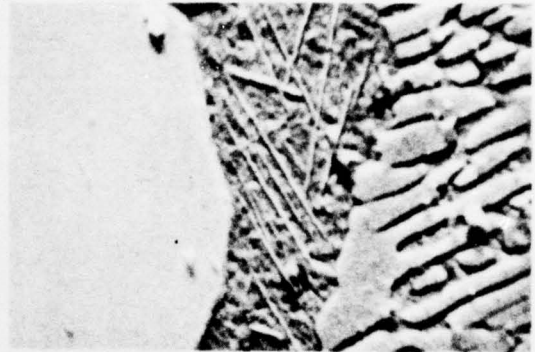


Figure 17. Cr-25Cb-34Al Ingot Directionally Solidified at 1.0 in./hr. with a Gradient of 200°F/in.

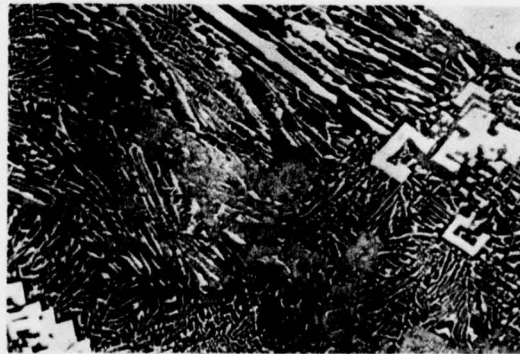




(a) Initial Region  
Magnification 100X



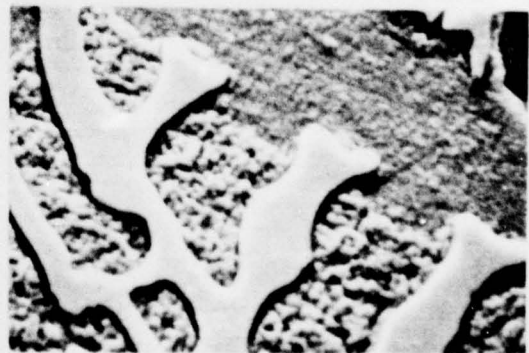
(b) Initial Region; SEM  
Magnification 2000X



(c) Final Region  
Magnification 100X

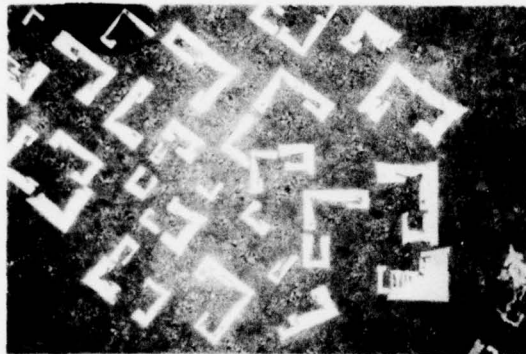


(d) Final Region; Polarized Light  
Magnification 500X



(e) Final Region; SEM  
Magnification 2000X

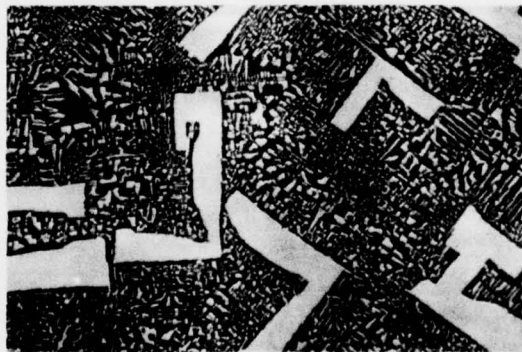
Figure 18. Transverse Sections From a Cr-25Cb-34Al Eutectic Alloy, Directionally Solidified at 1 in/hr. with a Gradient of 200°F/in.



(a) Transverse Section  
Magnification 30X



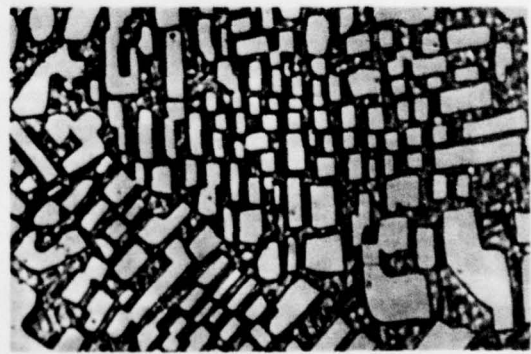
(b) Longitudinal Section;  
Polarized Light  
Magnification 30X



(c) Transverse Section  
Magnification 200X



(d) Longitudinal Section;  
Polarized Light  
Magnification 200X



(e) Transverse Section  
Magnification 1000X

Figure 19. Cr-25Cb-34Al Alloy Directionally Solidified at 1 in/hr. with a Gradient of 500°F/in.

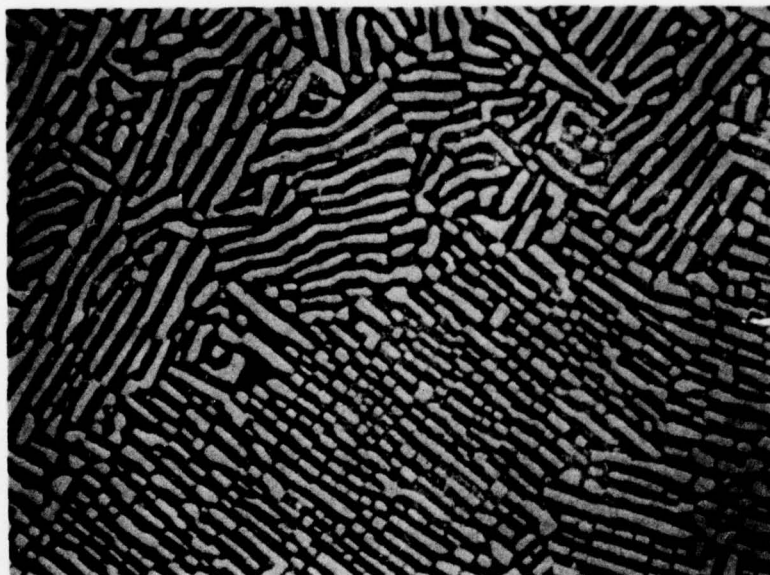
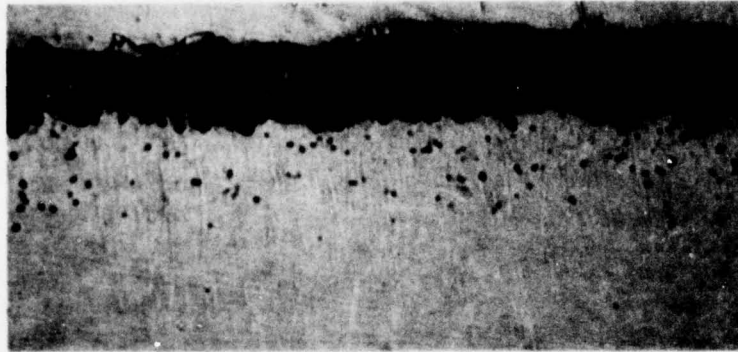


Figure 20. Cr-25Cb-34Al Directionally Solidified  
at 0.25 in/hr. in a Temperature Gradient  
of 900°F/in. Transverse Section  
Magnification 500X





(a) Hastelloy X

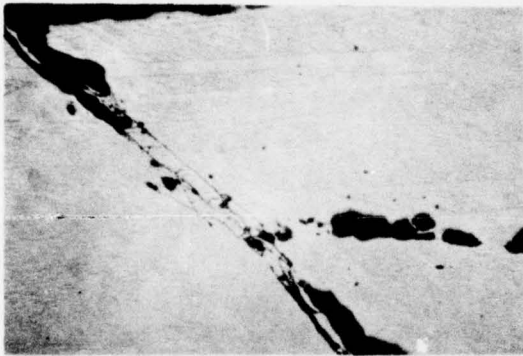


(b) Cr-25Cb-34Al As Cast

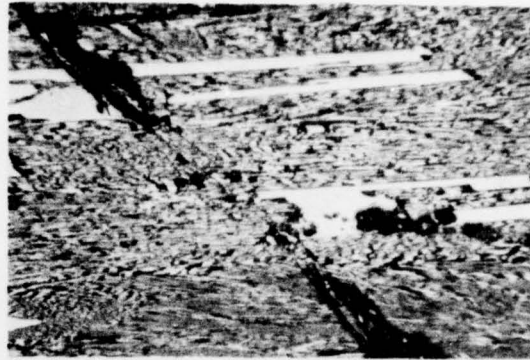


(c) Cr-25Cb-34Al Directionally Solidified at 3 in/hr.

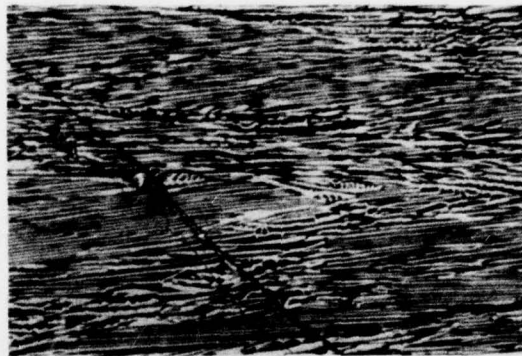
Figure 21. Transverse Sections from Alloys Oxidized at 2200°F for 5 hrs.  
Magnification 1000X



(a) Magnification 30X



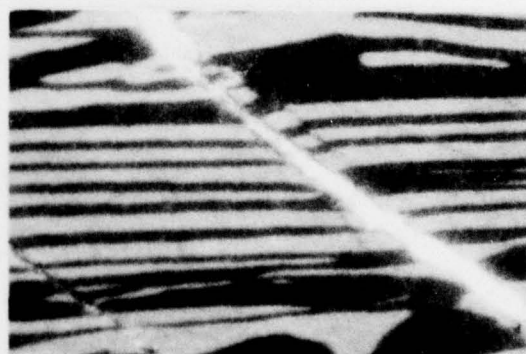
(b) Polarized Light, Magnification 30X



(c) Polarized Light, Magnification 100X



(d) Magnification 1000X



(e) Polarized Light, Magnification 1000X

Figure 22. Longitudinal Sections From a Cr-25Cb-34Al Alloy Fractured at Room Temperature

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